A TREATISE

ON THE

KINETIC THEORY OF GASES

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CAMBRIDGE:
AT THE UNIVERSITY PRESS
1899

PREFACE.

MY object in the following treatise is to apply to the Kinetic Theory of Gases a method of analysis different from that generally employed. It has been treated always on a certain fundamental assumption, namely, that the molecules of a gas are, as regards their relative motion, *independent of one another*. As a consequence, we may say as the expression, of that independence, the law of distribution of momenta assumes the exponential form ϵ^{-hQ}, and, so far as concerns translation velocities,

$$Q = \Sigma m (u^2 + v^2 + w^2),$$

m being mass, and u, v, w component velocities. From this independence and from this form of Q are deduced Boltzmann's theorems, namely the H theorem, and that of the equality of mean kinetic energy for each degree of freedom.

I propose to give to Q the more general form of a quadratic function, namely

$$Q = \Sigma m (u^2 + v^2 + w^2) + \Sigma\Sigma b (uu' + vv' + ww').$$

Here b is a negative function of the distance r at the instant considered between the two molecules whose velocities are u, u', etc., which function is inappreciable except for very small values of r. I shall endeavour to prove in Chapters IV., V. that without the b coefficients the motion cannot be stationary. It has been proved abundantly that, *assuming the independence*, the motion is stationary with the usual form of Q. I question the axiom, not the demonstration.

The consequence of attributing to Q the proposed new form is, that molecules near to each other have on average a motion in the same direction. They tend to form streams. That result, if it can be established, is worth investigation.

For ordinary gases under ordinary conditions the b coefficients are probably very small, and their effect negligible in such investigations as those of Tait and Boltzmann concerning diffusion, viscosity, etc. But I think that the law ϵ^{-hQ} in its altered form will express the state of the system without restriction as to density, except as follows. A physical limit there must be, when the gas liquefies under pressure, if not before. For it will not be contended that the distribution of momenta among the molecules of the liquefied gas is represented by the same exponential form as in the gaseous condition. An analytical limit there is, when Q in its altered form ceases to be necessarily positive, that is when the determinant of the coefficients ceases to be positive. It can be shown that this determinant does diminish as density increases, or temperature diminishes. But I have not calculated its value. It is therefore no more than a conjecture, though perhaps a plausible conjecture, that the vanishing of the determinant may coincide with the physical change in the substance.

It appears to me that the law of equality of mean kinetic energy for each degree of freedom cannot be reconciled with my proposed form of Q; that in fact the law holds only for the limiting case of a very rare gas.

It is no light thing to question a conclusion maintained by Boltzmann, if indeed he does maintain this conclusion for all substances, or for all gases irrespective of density. I can but state the objections to this theorem, and to a certain aspect of the H theorem, as they appear to me. The reader will judge what weight is to be attributed to them.

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10 *May*, 1899.

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CHAPTER I.

OUTLINE OF THE THEORY.

1. A GAS according to the Kinetic Theory consists of a great number of molecules in rapid motion. And the object of the theory is to explain on this hypothesis certain of the physical properties of gases.

Any quantity of gas which can be isolated for the purpose of experiments is to be regarded as containing a number of molecules practically infinite. It is not possible to control or to observe the motions of individual molecules. But the theory assumes that such motion is subject to the usual dynamical laws. Also that if the gas, as an aggregate of molecules, be at rest, no dissipation of energy takes place.

2. A molecule may consist of one or more than one atom according to the chemical constitution of the substance to which it belongs. It may be that hereafter we shall be able to explain on dynamical principles the chemical relations of atoms as constituent parts of a molecule, and of molecules *inter se*. And some progress has been made in this direction. At present the theory is concerned not with the chemical properties, but with those properties of gases which may change without any change taking place in the chemical composition of the gas: for instance, density, pressure, and temperature. And as depending on these latter, it is concerned with the phenomena of viscosity, diffusion, and conduction of heat or electricity.

3. A molecule moving as such, one and indivisible, has three degrees of freedom in respect of its motion of translation in space. And it may conceivably have three other degrees of freedom, namely, motion of rotation about its principal axes. In respect of its internal constitution it may have many degrees of freedom, but we know nothing of the internal constitution of molecules except what chemists tell us.

4. Any finite quantity of gas may, if protected from disturbance from without, retain for an indefinite time unimpaired its physical properties, for instance, its pressure and temperature, and also its chemical constitution. If therefore these properties are not changing, and are to be explained on dynamical principles as resulting from the motion of the molecules, such motion must be *stationary motion.*

OF HOMOGENEITY.

5. The gas, or system of molecules, may be in a certain sense *i.e.* if we regard all the molecules at any instant within a finite space, homogeneous For instance, a cubic centimetre of air has sensibly the same properties in all respects whether taken from one part of a horizontal table or from another part. It is true that it will generally not have in all respects the same properties if taken from near the floor, as if taken from near the ceiling. It will, namely, be heavier, *i.e.* will contain more molecules, in the former than in the latter case. That is because the air in the room is in a field of uniform force, gravity. But this force will not necessarily affect any other property of the gas, at all events under ordinary conditions to which it is subject.

If we assume the infinite divisibility of matter, or that any space, however infinitely small, contains an infinite number of molecules, the condition of homogeneity may apply to the molecules contained in any such infinitely small space. We may in that case say without ambiguity that the gas at a point P has the same properties as at another point Q.

6. Modern physicists however teach us that the molecules have finite dimensions, or that there is a finite distance, however small, within which two molecules cannot approach each other. That being the case, the homogeneity can be asserted only in the following form. If we consider a quantity of gas within a sphere of radius r described about P as centre, and a quantity within an equal sphere described about Q as centre, either sphere containing a number of molecules practically infinite, then r being within certain limits, the first quantity has the same physical properties as the second.

OF THE DENSITY OF A GAS.

7. The same doctrine of the finite size of molecules causes considerable difficulty in defining certain other properties of the system, for instance *the density*.

The density of the gas is usually defined to be the sum of the masses of all the molecules in unit of volume. But if the molecules have finite dimensions, that may make the density at any point relative to that at other points depend on the unit arbitrarily chosen. It is not therefore a complete definition. We can however say, and it is generally sufficient for our purpose,

(*a*) If there be N molecules within a definite volume S, the average density at any point within S is N/S.

(*b*) Again, we can define the density at a point which answers some general description, or as we may call it the relative density. For instance, suppose f to be a continuous function of the position of a point, then we may define the density with reference to f, as for instance at points where $f=0$, provided that there exists an infinite number of such points. For consider any n of them, and about each a small sphere of volume ω. Let $n\omega$ be the unit of volume. Let N be the number of molecules supposed of equal mass which, or the centres of inertia of which, are within some one or other of these small spheres. Then the density where $f=0$ is $N/n\omega$ in the limit, as n is increased indefinitely, $n\omega$ remaining constant.

To define density *at a point*, as a function of the coordinates of that point, is with finite molecules a more difficult matter.

Let r be a line of any arbitrary fixed length. As a first step to our definition, let us say the density at a point P, or x, y, z is the number of molecules, supposed of equal mass, contained within a sphere of radius r described about P as centre, divided by the volume of that sphere. If n be that number, ρ the density, then our definition is

$$\rho \text{ at } P = \frac{3n}{4\pi r^3}.$$

But that makes ρ generally a function of r as well as of x, y, z. How are we to get rid of r? Boltzmann and other writers after or before him would complete the definition thus, ρ at $P = \dfrac{3n}{4\pi r^3}$ *when r becomes infinitely small*, any space however infinitely small being assumed, for this purpose only, to contain an infinitely great number of molecules. This definition does not materially differ from that which we should give if our gas, instead of consisting of discrete molecules, were a continuous fluid, any portion of which may be conceived as infinitely subdivided.

But it is inconsistent with the teaching of these same writers, who maintain that molecules have finite dimensions, that in fact we can ascertain limits between which those dimensions must lie. It may be admitted that no ill consequences have yet arisen from the use of this inconsistent definition, and if it be either necessary or useful, the inconsistency need not be regarded as a serious objection. Inconsistency may indeed be an advantage in mathematics as it often is in politics. It may be admitted also that this definition occurs to us by instinct when we are asked to define density at a point. That may be because we have passed through a former state of existence in which matter was supposed to be continuous, and therefore the definition strictly accurate. And our instinctive resort to it is due to unconscious memory of that former state.

8. We may avoid the difficulty by making a further assumption with regard to the properties of our system. Let

r_0 be the radius of a sphere described about P as centre which contains a very great number of molecules. Let r_1 be greater than r_0 in a finite ratio. Let as before n be the number of molecules within a sphere of radius r. Now let us assume, as a property of our system, that for all values of r between r_0 and r_1, the ratio $n : r^3$ is constant. Then we may define ρ at P as $\frac{3n}{4\pi r^3}$, using this constant value of n/r^3.

This method implies either that the state of our gas does not change from point to point in space, or that it changes so gradually as to be sensibly constant throughout the space between the spheres of radii r_0 and r_1.

9. Assuming that the state of our gas changes so rapidly in space that we cannot make the above assumption, and assuming that we scruple to base our definition on an assertion which we elsewhere contradict, it seems to me that the expression "density at a point" or "number of molecules per unit of volume at a point" has of itself no meaning whatever when the molecules are of finite dimensions, but a meaning may be given it in an arbitrary way. One way would be to take an arbitrarily chosen volume for the unit. I would suggest the following as the best form of definition. Let f be a continuous positive function of r which is equal to unity for all values of r less than a certain distance a, and for which $\frac{df}{dr}$ is always negative when $r > a$, and such that $\int_a^\infty r^2 f dr$ is a convergent series. Then define the density at P as Σmf, r being measured from P, m being the mass of a molecule and the summation including all molecules in space. For with molecules of finite dimensions, density at P must depend upon the distances of many molecules from P, but cannot be affected by those whose distances from P are very great.

THE STREAM VELOCITY.

10. As with the density, so precisely the same difficulty presents itself if we try to define the *stream velocity*, or in

Professor Tait's language, *mass motion*, of the gas in given direction at any point P. M. Ladislas Natanson in a paper, to which I shall refer later, makes use of this function without giving any definition of it except by calling it "vitesse moyenne ou apparente." He is however, as I understand, willing to assume that any infinitely small space contains an infinite number of molecules. As the same difficulty arises, so the same solution *mutatis mutandis* may be resorted to, as in the case of density.

OF THE PRESSURE OF A GAS.

11. The motion which we attribute to our molecules cannot, assuming the gas to be at rest relatively to the surrounding space, be related to any particular direction in space. That is, at or near any point P there are on the average of time as many molecules moving with given velocity in any one direction as in any other. For if otherwise the pressure of the gas would, as shown by the next paragraph, be unequal in different directions, which is known not to be the case if the gas be at rest.

12. Assuming the property mentioned in the last paragraph, and assuming the distribution of momentum among the molecules to be known, we can calculate the quantity of momentum transferred across an imaginary plane within the gas per unit of area and time. Let m be the mass of a molecule, ρ the number of molecules per unit of volume, to be defined as above explained, and $\rho f(V)\,dV$ the number per unit of volume whose velocity of translation lies between V and $V + dV$. Then by our assumption the number of these last whose direction of motion makes with the normal to the plane angles between θ and $\theta + d\theta$ is

$$\tfrac{1}{2}\rho\,.f(V)\,dV\sin\theta d\theta.$$

Their velocity normal to the plane is $V\cos\theta$. Therefore the quantity of momentum normal to the plane transferred across the plane in one direction per unit of area and time by molecules having velocity $V \dots V + dV$ is

$$\tfrac{1}{2} m\rho V^2 \int_0^{\frac{\pi}{2}} \sin\theta \cos^2\theta d\theta = \tfrac{1}{6} m\rho V^2.$$

And the quantity of momentum so transferred by all the molecules is

$$\tfrac{1}{6} m\rho \int_0^\infty V^2 f(V) dV$$

$$= \tfrac{1}{6} m\rho \overline{V^2} \text{ suppose,}$$

$\overline{V^2}$ being the mean value of V^2 for all the molecules.

13. If further the molecules exert on one another no forces, twice the quantity of momentum so transferred through unit of area of the plane is the normal *pressure* of the gas per unit of area of the plane. See Watson's *Kinetic Theory of Gases*, second edition, pp. 56—58.

For we may suppose the gas confined in a vertical cylinder under a heavy moveable piston from which molecules striking rebound as elastic bodies. The momentum normal to the base of the piston, *i.e.* vertically upwards, which if it were an imaginary plane would be transferred through it, is in fact, the mass of the piston being very great, reversed, so that twice that quantity is transferred to the piston, and tends to make the piston rise in the cylinder. That is, the piston receives per unit of area and time from the impacts of the molecules momentum equal to $\tfrac{1}{3} m\rho \overline{V^2}$ vertically upwards. It also acquires by the action of gravity per unit of area and time momentum Mg vertically downwards, where g is the force of gravity, and M bears to the whole mass of the piston the same ratio which unit of area bears to the base of the piston. For equilibrium

$$Mg = \tfrac{1}{3} m\rho \overline{V^2} = p, \text{ the pressure per unit of area.}$$

If the impacts of the molecules be sufficiently numerous per unit of time the piston will remain sensibly at rest.

OF THE TEMPERATURE OF A GAS.

14. We have then in the absence of intermolecular forces

$$p \text{ varies as } \rho \overline{V^2}.$$

If the molecules do exert mutual forces on one another, the above value of the pressure is not accurate. But there are sufficient reasons for believing that for ordinary gases under ordinary conditions the pressure is not materially affected by the intermolecular forces. For such gases therefore, accurately or approximately,

$$p \text{ varies as } \rho V^2.$$

But for such gases, accurately or approximately, the laws of Boyle and Charles hold good, whence p varies as $\rho\theta$, θ denoting the *absolute temperature*. It is thence inferred that, accurately or approximately, θ varies as V^2. And that statement we must accept provisionally. Temperature measured from the absolute zero is represented by the mean square of the velocity of translation. On this theory temperature is a quality which cannot be attributed to a molecule, but only to an aggregate of molecules.

OF INTERMOLECULAR FORCES.

15. It is however certain that for sufficiently dense gases intermolecular forces do exist, and we must now make a further assumption regarding them. We shall assume, namely, that the intermolecular force R between two molecules

(1) Acts in the line joining their centres of inertia, or within very small limits of error may be regarded as so acting.

(2) Is a continuous function of the distance r between those centres of inertia, which becomes evanescent for all values of r exceeding a very small finite distance r_0, which distance again is negligible compared with the dimensions of any mass of gas upon which we can make experiments.

(3) The force must for sufficiently small values of r become repulsive, and should become infinite as r is indefinitely diminished—but save for these restrictions it may be that the force is attractive for some values and repulsive for other values of r.

R shall be taken as positive when repulsive.

If c be the smallest radius beyond which the force exerted by a molecule at the centre on another molecule is negligible, c is defined to be the *radius of action* of the central molecule, and a sphere of radius c described about the molecule is its *sphere of action*, or its *effective volume.*

THE FUNDAMENTAL ASSUMPTION.

16. As above stated, the number of molecules of our gas per unit of volume may be different at different points of the system considered. Representing by ρ that number, we may have to treat ρ as a function of x, y, z. At present it is convenient to treat only the case in which ρ is constant throughout the system, and the distribution of velocities among the molecules is the same throughout the system. That being the case we may define as follows.

At any instant let $\rho f_x(u)\,du$ be the number per unit of volume of molecules whose component velocities in the direction taken for x lie between u and $u+du$. Similarly let $\rho f_y(v)\,dv$ be the number per unit of volume whose component velocities in direction y lie between v and $v+dv$, and $\rho f_z(w)\,dw$ the number whose component velocities in direction z lie between w and $w+dw$.

We might say, and it would be precisely equivalent to what we have already said, that $f_x(u)\,du$ is *the chance that* a given molecule shall have velocity in x between u and $u+du$, and $f_y(v)\,dv, f_z(w)\,dw$ are the corresponding chances for y and z.

17. These definitions, however apparently unambiguous, may be based upon either of two diametrically opposite assumptions.

We may make namely, *assumption A.*

A. The chance of any molecule having velocity in x between u and $u+du$ is independent, not only of its position in space, but also of the velocities v, w, which it has in directions y and z, and further except in the case mentioned below, it is independent of the positions and velocities at the instant of all the other molecules of the system. The excepted case is when the two molecules are so placed that they are, or very recently have been, within one another's sphere of action. The force of this exception, and the necessity for it, will appear in the consideration of the H theorem, Chapter III.

On that assumption it follows that the chance of any given molecule having at any given instant velocities in x, y, z respectively between u and $u + du$, v and $v + dv$, w and $w + dw$, is

$$f_x(u)\,f_y(v)\,f_z(w)\,du\,dv\,dw.$$

Further, if we consider any pair of molecules, and denote by the suffix 1 quantities relating to the first, by the suffix 2 quantities relating to the second, then the chance that they shall at any instant respectively have velocities

$$\begin{array}{rll} \text{in } x \text{ between} & u_1 \text{ and } u_1 + du_1, \\ & u_2 \text{ and } u_2 + du_2; \\ \text{in } y \text{ between} & v_1 \text{ and } v_1 + dv_1, \\ & v_2 \text{ and } v_2 + dv_2; \\ \text{and in } z \text{ between} & w_1 \text{ and } w_1 + dw_1, \\ & w_2 \text{ and } w_2 + dw_2, \end{array}$$

is

$$f_{1x}(u_1)\,f_{1y}(v_1)\,f_{1z}(w_1)\,f_{2x}(u_2)\dots du_1dv_1dw_1du_2\dots dw_2.$$

This or its equivalent is the assumption on which the kinetic theory of gases has hitherto generally been treated*. I shall refer to the state of things assumed as *condition A*. Without doubt it may be assumed legitimately with respect to the limiting case of an infinitely rare gas, that is one in which

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* Dr Watson (*Kinetic Theory of Gases*, 2nd Edition, p. 3, equation B) assumes the independence of the chances for two spheres *approaching collision*. And that is sufficient for his purpose. Professor Tait ("Foundations of the Kinetic Theory of Gases," *Transactions R. S. Edinburgh*, 1888, Art. 21) makes an equivalent assumption. Dr Boltzmann (*Vorlesungen über Gas Theorie*, Part I, p. 23) assumes that the motion is, and ever continues to be, "molecular-ungeordnet." I shall consider later (Chapter III.) what may be the effect of that assumption. In the meantime the weapon that Dr Boltzmann draws from that armoury is precisely the same as the one used by Watson and Tait, namely, that for all pairs of spheres or molecules *approaching collision* the chances are independent, as stated in my condition A. These writers do not define the exception, the occasion for definition not having arisen, but they do not assert the independence in the excepted case.

the dimensions of any molecule, or if it be a centre of force, its radius of action, are negligible compared with the mean distance between any molecule and its nearest neighbour. It is probable also that all the known gases under ordinary conditions of pressure and temperature, approximate closely to the limiting condition of infinite rarity. And therefore the calculations made on the assumption of condition A or its equivalent by Tait, Boltzmann, and others, of the rate of diffusion, conduction of heat or electricity, &c., for such gases remain unaffected.

18. Or we may make *assumption B.*

B. The chance of a given molecule having at any instant assigned velocities is **not** independent of the positions and velocities of all the other molecules at the instant. On this assumption B, instead of deducing the chance of the members of a group of n molecules having respectively at any instant the velocities

$$u_1 \dots u_1 + du_1 \text{ \&c.}$$

from the assumed chances for individual molecules, we must reverse the process. Let the chance that at the given instant the coordinates of the n molecules shall lie respectively between

$$x_1 \text{ and } x_1 + dx_1,$$
$$y_1 \text{ and } y_1 + dy_1,$$
$$z_1 \text{ and } z_1 + dz_1;$$

for the first molecule,

$$x_2 \text{ and } x_2 + dx_2,$$
&c.

for the second, and so on,

and their component velocities between

$$u_1 \text{ and } u_1 + du_1,$$
$$v_1 \text{ and } v_1 + dv_1,$$
$$w_1 \text{ and } w_1 + dw_1;$$

for the first molecule,

$$u_2 \text{ and } u_2 + du_2$$

for the second and so on, be denoted by

$$F(x_1 y_1 \ldots z_n u_1 v_1 \ldots w_n)\, dx_1 dy_1 \ldots dw_n.$$

Then the chance that the x velocity of the first molecule shall lie between

$$u_1 \text{ and } u_1 + du_1,$$

whatever be the positions and velocities of the other $n-1$ molecules, is

$$\iiint_{-\infty}^{+\infty} (dx_1 dx_2 \ldots dz_n dv_1 dw_1 du_2 \ldots dw_n)\, F(x_1 y_1 \ldots u_1 \ldots w_n).$$

19. By way of illustration let us suppose, under condition A,

$$f(u) = C\epsilon^{-hu^2},$$

where C is the usual constant, chosen so that

$$C\int_{-\infty}^{\infty} \epsilon^{-hu^2}\, du = 1.$$

Then on assumption A the chance that the members of the group of n molecules supposed to be of equal masses, shall respectively have their coordinates and velocities between the above limits is of the form

$$C\epsilon^{-hQ} dx_1 \ldots dz_n du_1 \ldots dw_n,$$

where $\qquad Q = \Sigma\,(u^2 + v^2 + w^2)$, and h is constant ;

and in dealing with assumption B, let us assume, the molecules being all of the same mass and the same structure,

$$F(x_1 y_1 \ldots u_1 \ldots w_n) = C\epsilon^{-hQ},$$

where

$$\begin{aligned} Q = {} & u_1^2 + v_1^2 + w_1^2 + u_2^2 + \ldots + w_n^2\,; \\ & + b_{12}(u_1 u_2 + v_1 v_2 + w_1 w_2) \\ & + b_{13}(u_1 u_3 + v_1 v_3 + w_1 w_3) + \&c. \end{aligned}$$

Here the b coefficients shall be functions of the distance r, at the instant between the pair of molecules to which the suffixes relate, which functions become evanescent when r exceeds a certain very small distance. In that case omitting the constant

$$\begin{aligned} f(u_1) &= \iiint_{-\infty}^{+\infty} \epsilon^{-hQ}\, dx_1 \ldots dz_n dv_1 dw_1 du_2 \ldots dw_n \\ &= \epsilon^{-\frac{D}{2D_{11}} h u_1^2}, \text{ as shown in the Appendix } (g). \end{aligned}$$

Here D is the determinant of n^2 constituents

$$D = \begin{vmatrix} 2 & b_{12} & b_{13} & \dots \\ b_{12} & 2 & b_{23} & \dots \\ b_{13} & b_{23} & 2 & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix}$$

and D_{11} is its first coaxial minor.

The form of $f(u)$ under assumption B is the same, except for the factor of h, as under assumption A, but the physical state of the system may be very different. For instance, under assumption B, two molecules at a distance r apart, so small that the corresponding b is not negligible, are, if b be negative, on average moving in the same direction. According to Boltzmann (*Vorlesungen*, p. 21) the motion in this case is not "molecular ungeordnet."

20. Of these two assumptions A and B, B includes A as a particular case. It is therefore better, if and in so far as it may turn out to be possible, to establish a proposition on assumption B, rather than on assumption A. My object in the present treatise is to show that it is generally possible. It will appear also that A requires us to assume our gas to be infinitely rare, whereas B imposes upon us no stringent condition with regard to the density. The only condition in fact which appears to be required at present is this: the coefficients b must be such that for all possible values of the u's, v's, and w's, Q shall be positive. Mathematically that is expressed by saying that the determinant D and all its coaxial minors must be positive.

D will appear to be generally a function of density and temperature, and if ever $D=0$ the mathematical treatment changes, whether or not the physical system changes its state, and if so whatever the nature of that change may be.

It will appear also that if u, v, w be the component velocities of a molecule of mass m, u', v', w' those of any other molecule,

$$\tfrac{1}{2}m\,(\overline{uu'} + \overline{vv'} + \overline{ww'})$$

is related to *the Virial* defined in Chapter II. of the intermolecular forces acting on m. See Arts. 58, 85.

CHAPTER II.

CLAUSIUS' THEOREM.

21. It will be necessary to consider at length later the law of distribution of velocities or momenta among the molecules for any given value of the mean kinetic energy—that is the form of the function which we denoted above, Art. 12, by $f(V)$. The following proposition, due originally to Clausius, is independent of that law.

If m be the mass of any one of a system of molecules in stationary motion, x, y, z the coordinates of its centre of inertia at any instant, we have, Σ denoting summation for all the molecules of the system, and Σmx, Σmy, Σmz being zero

$$\frac{d}{dt}\left(\Sigma mx\,\frac{dx}{dt}\right) = 0,$$

$$\frac{d}{dt}\left(\Sigma my\,\frac{dy}{dt}\right) = 0,$$

$$\frac{d}{dt}\left(\Sigma mz\,\frac{dz}{dt}\right) = 0,$$

or

$$\Sigma m\left(\frac{dx}{dt}\right)^2 + \Sigma mx\,\frac{d^2x}{dt^2} = 0,$$

with similar equations for y and z.

It follows that

$$\Sigma m\left\{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right\} = -\Sigma(Xx + Yy + Zz),$$

X, Y, Z being the component forces, whether external or intermolecular, acting on a molecule.

22. We will now however reserve X, Y, Z for the components of external force only, and let R be the intermolecular force between two molecules acting in the line joining their centres, and let R_x, R_y, R_z be its components. So that Clausius' equation becomes

$$\Sigma m\left(\left(\frac{dx}{dt}\right)^2+\left(\frac{dy}{dt}\right)^2+\left(\frac{dz}{dt}\right)^2\right)=-\Sigma(Xx+Yy+Zz)$$
$$-\Sigma\Sigma(R_x x+R_y y+R_z z)\ldots\ldots\ldots(1).$$

Half the expression on the right-hand side of the last equation is called the Virial. And separately

$$-\tfrac{1}{2}(Xx+Yy+Zz)$$

is the Virial of the external forces, and $-\frac{1}{2}\Sigma\Sigma(R_x x+R_y y+R_z z)$ is the Virial of the intermolecular forces.

23. Let one molecule be at P or x, y, z, another at P' or x', y', z'. Let $r^2=(x-x')^2+(y-y')^2+(z-z')^2$. Then for the force on P due to P', R being taken as positive when repulsive,

$$R_x=\frac{x-x'}{r}R,\quad R_y=\frac{y-y'}{r}R,\quad R_z=\frac{z-z'}{r}R.$$

Similarly for the force on P' due to P,

$$R_x=-\frac{x-x'}{r}R,\quad R_y=-\frac{y-y'}{r}R,\quad R_z=-\frac{z-z'}{r}R,$$

and therefore for two molecules at P and P'

$$\Sigma(R_x x+R_y y+R_z z)=R\,\frac{(x-x')^2+(y-y')^2+(z-z')^2}{r}=Rr.$$

And so the term in Clausius' equation due to the intermolecular forces is

$$\Sigma\Sigma(R_x x+R_y y+R_z z)=\Sigma\Sigma Rr\ \ldots\ldots\ldots\ldots(2),$$

each pair of molecules being counted once.

24. We have next to consider the external forces, whose components are X, Y, Z. I shall follow Van der Waals' method.

Let the whole system be enclosed by a surface S, through which the molecules cannot pass. Let p be the normal pressure per unit of area on S, directed inwards. At any point P on S let λ, μ, ν be the direction cosines of the normal s to S at P, l, m, n those of a the line joining P with the origin. Then for a molecule at P

$$\begin{aligned}-(Xx+Yy+Zz) &= p\,(l\lambda a+m\mu a+n\nu a)\\ &= pa\cos(s,\,a)\\ &= pa\frac{da}{ds},\end{aligned}$$

if ds be an element of the normal, measured outwards,

$$= \tfrac{1}{2}p\,\frac{da^2}{ds}.$$

Let us now assume p to be constant over the whole surface S. Then

$$\begin{aligned}&-\iint(Xx+Yy+Zz)\,dS\\ &= \tfrac{1}{2}p\iint\frac{da^2}{ds}\,dS\\ &= \tfrac{1}{2}p\iiint\nabla^2a^2\,dx\,dy\,dz\end{aligned}$$

throughout the space enclosed by S, by Green's Theorem,

$$= 3p\omega,$$

if ω be the volume enclosed by S.

We see then that the Virial

$$= \tfrac{3}{2}p\omega-\tfrac{1}{2}\Sigma\Sigma Rr,$$

or by (1) $$\tfrac{3}{2}p\omega=\Sigma\tfrac{1}{2}m\,(u^2+v^2+w^2)+\tfrac{1}{2}\Sigma\Sigma Rr \quad\text{.........(3)};$$

or, if T be the mean kinetic energy of the system of molecules,

$$p=\tfrac{2}{3}\frac{T}{\omega}+\tfrac{1}{3}\Sigma\Sigma Rr/\omega,$$

and $\dfrac{T}{\rho\omega}$ represents the mean kinetic energy of a molecule.

If we take the volume ω for a generalised coordinate, supposing it to change in magnitude but not in shape, the other coordinates of the system may be $x\omega^{\frac{1}{3}}$, $y\omega^{\frac{1}{3}}$, &c., where x, y, &c. are numerical. Then $\frac{2}{3}\frac{T}{\omega} = \frac{dT}{d\omega}$, and if χ be the potential of the intermolecular forces $\frac{1}{3}\Sigma\Sigma Rr/\omega = -\frac{d\chi}{d\omega}$, and our equation assumes the Lagrangian form $p = \frac{dT}{d\omega} - \frac{d\chi}{d\omega}$, p being the applied force which maintains ω constant.

25. If the surface S be an imaginary closed surface, the system of molecules in the external space being homogeneous with the system within S, the pressure per unit of area of S is given by the above equation,

$$\tfrac{3}{2}p\omega = \Sigma\tfrac{1}{2}m\,(u^2 + v^2 + w^2) + \tfrac{1}{2}\Sigma\Sigma Rr.$$

The whole Virial or $\frac{3}{2}p\omega - \frac{1}{2}\Sigma\Sigma Rr$ is thus equal to the whole mean kinetic energy of the molecules within S. It does not follow that the two parts of the Virial, namely $\frac{3}{2}p\omega$ and $-\Sigma\Sigma\frac{1}{2}Rr$, are separately proportional to $\Sigma\frac{1}{2}m\,(u^2 + v^2 + w^2)$.

26. If S be the external elastic boundary of the system through which molecules cannot pass, we might calculate p by the same method as we calculated it in the case of there being no forces, namely $p = \frac{1}{3}m\rho' V'^2$, where ρ' is the mean density, and $\frac{1}{2}mV'^2$ the mean kinetic energy, of molecules near S. This result is not inconsistent with Art. 24, because the mean potential energy near S is, in the case now supposed, different from the mean potential energy throughout the enclosed space, $\overline{V^2}$ and so $\overline{V'^2} \neq \overline{V^2}$ and $\rho' \neq \rho$.

The value of $\Sigma\Sigma Rr$ for Elastic Spheres.

27. We have assumed R to be a finite force. In the limiting case of so-called elastic bodies, the force which acts in collision between two such bodies is, according to the usual convention, an infinite force which reverses the velocities of the colliding bodies normal to their tangent plane at collision in an infinitely short time. As a consequence of the time being infinitely short, no change takes place in the coordinates during

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collision, and no body can ever be in collision with more than one other body at the same instant.

It is of course admitted that no such body exists in nature. But the behaviour of gas molecules in regard to their mutual action is probably, at least in the case of rare gases, approximately the same as it would be if they were elastic spheres of this form. And the assumption made in the case of the spheres that the kinetic energy of translation of two spheres in collision is in the aggregate unchanged by the collision, must if molecules are stable be true on average for any form of molecule.

28. It is then possible to calculate $\Sigma\Sigma Rr$ for a system of elastic spheres, regarding the force as finite, and sufficiently great to produce the reversal of the normal velocities in a finite time τ, and treating the coordinates as constant, to proceed to the limit when the force becomes infinite, and τ zero.

Let the colliding spheres be each of mass m, and of diameter c. Let ρ be the number of spheres per unit of volume.

Let T be now the mean kinetic energy of a sphere. And let u, v, w, u', v', w', be the component velocities of any two spheres, V their relative velocity. Then

$$V^2 = (u - u')^2 + (v - v')^2 + (w - w')^2,$$

and

$$m\overline{V^2} = 2m\,(\overline{u^2} + \overline{v^2} + \overline{w^2}) \text{ on average}$$

$$= 4T.$$

Let θ be the angle between the relative velocity and the line of centres at collision. Then for each sphere the normal component of relative velocity is $\frac{1}{2}V\cos\theta$, and it is reversed in time τ. The assumed force is then $R = mV\cos\theta/\tau$, and it acts during the time τ. The number of collisions per unit of volume and time is, given V, $\pi c^2 V\rho$. And the number for which θ lies between θ and $\theta + d\theta$ is

$$2\pi c^2 V\rho \sin\theta \cos\theta d\theta.$$

Also $r = c$. Hence for all collisions of a pair of spheres with given V

$$\Sigma Rr = 2\pi mc^3 V^2 \rho \int_0^{\frac{\pi}{2}} \sin\theta \cos^2\theta d\theta$$

$$= \tfrac{2}{3}\pi mc^3 V^2 \rho.$$

And for all collisions of a pair of spheres with whatever value of V

$$\Sigma \overline{Rr} = \tfrac{2}{3}\pi c^3 \rho m \overline{V}^2$$

$$= \tfrac{8}{3}\pi c^3 \rho T,$$

or

$$\tfrac{1}{2}\Sigma Rr = \tfrac{4}{3}\pi c^3 \rho T.$$

But each collision is now counted twice, namely, once from the point of view of each of the spheres concerned. Counting each collision once, or from the point of view of one sphere only,

$$\tfrac{1}{2}\Sigma Rr = \tfrac{2}{3}\pi c^3 \rho T \text{.......................} (4),$$

whence we obtain for each sphere

$$\frac{d}{d\rho}\tfrac{1}{2}\Sigma Rr = \tfrac{2}{3}\pi c^3 T,$$

and for all spheres

$$\frac{d}{d\rho}\tfrac{1}{2}\Sigma\Sigma Rr = \tfrac{2}{3}\pi c^3 \rho T,$$

and therefore

$$\tfrac{1}{2}\Sigma\Sigma Rr = \tfrac{1}{2}\,\tfrac{2}{3}\pi c^3 \rho \,.\, \rho T.$$

I shall write κ for $\tfrac{2}{3}\pi c^3 \rho$. If a be the radius of a sphere which on average contains one molecule, evidently

$$\kappa = \tfrac{1}{2}\frac{c^3}{a^3},$$

or κ is four times the aggregate volume of all the spheres in unit of volume.

It follows from Art. 24 that

$$\tfrac{3}{2}p\varpi = \Sigma\tfrac{1}{2}m(u^2 + v^2 + w^2) + \Sigma\tfrac{1}{2}\kappa T,$$

or

$$p = \tfrac{2}{3}(1 + \tfrac{1}{2}\kappa)\rho T \text{ ....} (5).$$

On a system of Elastic Spheres in Vertical Column.

29. The following investigation depends upon the usual assumption made with respect to collisions between elastic bodies, that a certain momentum is instantaneously transferred through a finite space. The responsibility for that assumption rests on the inventor, whoever he was, of the theory of rigid elastic bodies. Consider a vertical column of gas, or material system, whose molecules are equal elastic spheres, under a constant vertical force f.

If p be the pressure per unit of surface, x the height of a point in the column above a fixed plane, m the mass of a sphere, ρ the density, ρ_0 the density at the base, we have

$$\frac{dp}{dx} = -mf\rho,$$

also by (5) $$p = \tfrac{2}{3}(1 + \tfrac{1}{2}\kappa)\,\rho T.$$

Whence, if we make

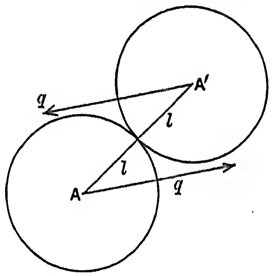
$$T = \text{constant} = \frac{3}{4h},$$

we find $$-2mfh = \frac{d \log \rho}{dx} + \tfrac{2}{3}\pi c^3 \frac{d\rho}{dx},$$

or $$\rho = \rho_0 \epsilon^{-2hmfx} \epsilon^{-(\kappa - \kappa_0)}.$$

Again, consider N spheres crossing the plane $x = 0$ with u for vertical component of velocity. Of these some, say $N - N'$, will reach the plane $x = dx$ without collision. N' will undergo collision before reaching dx. But for these N' there will in stationary motion be substituted, as the result of collisions, N' other spheres with the same vertical component u.

Now, if the impact were direct, *i.e.*, the line of centres at collision vertical, the effect of the collision would be to substitute for a molecule with vertical velocity u at height x a molecule with the same vertical velocity u at height $x + c$, where c is the diameter, or, as we may express it, the substituted sphere would gain a vertical height c, without losing in respect of that distance any kinetic energy to the force f. We might without affecting the general motion suppose the two spheres to change places



after collision, so that one would lose, and the other gain, the height c without change of kinetic energy. If, therefore, all the N' collisions were direct, the average height of the N spheres or their substitutes at the end of the time $\frac{dx}{u}$ would be, not dx, but $dx + \frac{N'}{N}c$, while their loss of kinetic energy would be $Nmfdx$.

But all impacts will not be direct; we must consider then the result of indirect impacts. For this purpose consider two classes of collisions, in one of which the sphere A has vertical component u before collision, and in the other A' has vertical component u after collision. The effect of a pair of collisions one from each class, is to substitute A' for A as the sphere with vertical component u. Now let l (see figure) denote the vector line of centres at collision, and $\cos(ul)$ the cosine of the angle which l makes with the vertical. Then in the first of the pair of collisions the centre of A is below the point of contact by $\frac{1}{2}c\cos(ul)$. In the second, the centre of A' is above the point of contact by $\frac{1}{2}c\cos(ul)$. There is no reason why the point of contact should be higher or lower in one case than in the other. It will be on average at the same height. Therefore on average of all pairs of collisions substituting A' for A with vertical velocity u, A' is above A by

$$c\,\overline{\cos(ul)} = r, \text{ suppose.}$$

Let q be the relative velocity of the two colliding spheres. Then considering q as radius vector of a cone of axis u, and l as radius vector of a cone of axis q, we get

$$r = c\,\overline{\cos(uq)\cos(ql)}$$
$$= \tfrac{2}{3}c\,\overline{\cos(uq)},$$

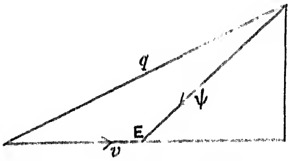
because $$\overline{\cos(ql)} = \int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta\, d\theta \Big/ \int_0^{\frac{\pi}{2}} \cos\theta \sin\theta\, d\theta = \tfrac{2}{3}.$$

Let v be the absolute velocity of the sphere whose vertical component of velocity is u, so that

$$\cos(uv) = \frac{u}{v}.$$

Then
$$r = \tfrac{2}{3}c\,\overline{\cos(uq)}$$
$$= \tfrac{2}{3}c\,\frac{u}{v}\cos(vq).$$

Let ψ be the velocity of the other colliding sphere, E the angle between v and ψ. Then



$$r = \tfrac{2}{3}c\,\frac{u}{v}\,\frac{v-\psi\cos E}{q}.$$

We have to multiply this by the number of collisions which N spheres having velocity v undergo with spheres of velocity $\psi \ldots \psi + d\psi$, making with v angles $E \ldots E + dE$ in time dt, or $\frac{dx}{u}$, and then integrate for all values of ψ and E.

Let $\rho f(\psi)\,d\psi$ be the number of spheres in unit volume with velocity $\psi \ldots \psi + d\psi$. The result is

$$N\pi c^2\rho\int_0^\infty d\psi f(\psi)\int_0^\pi \tfrac{1}{2}\sin E\,dE\,q\,\tfrac{2}{3}c\,\frac{u}{v}\,\frac{v-\psi\cos E}{q}\,\frac{dx}{u}$$
$$= \tfrac{2}{3}\pi c^3\rho \,.\, N dx$$
$$= \kappa N dx.$$

Therefore at time dt the average height of the N spheres or their successors above the plane $x = 0$ is $(1+\kappa)\,dx$.

But the energy which allowing for substitutions they lose in the ascent is $Nmfdx$. The loss takes place only during free path. It follows that the loss of energy due to the ascent dx is, allowing for substitutions, $mfdx\,(1-\kappa)$ per sphere.

Now suppose that at $x = 0$ the number per unit of volume of spheres having $\tfrac{1}{2}mu^2 \ldots d(u^2)$ for energy of vertical velocity is

$$K\epsilon^{-hmu^2}\,d(u^2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(a),$$

where K is constant. Then, by what has been proved above, the number which at height ∂x have $\tfrac{1}{2}mu^2 \ldots d(u^2)$ for energy of vertical velocity is

$$\epsilon^{-2hmf\partial x}\epsilon^{-\partial\kappa}\,K\epsilon^{-hmu^2}d(u^2),$$

and the number which at height ∂x have

$$\tfrac{1}{2}mu^2 \ldots d\,(u^2) - mfdx\,(1-\kappa)$$

for energy of vertical velocity is

$$\epsilon^{-2hmf\partial x}\epsilon^{-\partial\kappa}\,K\epsilon^{-h\,(mu^2-2mf\partial x)\,(1-\kappa))}\,du^2,$$

that is, $$K\epsilon^{-hmu^2}\,du^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(b),$$

because, neglecting κ^2, &c.,

$$\kappa = \kappa_0\epsilon^{-2hmfx},$$

and therefore $$2hmf\kappa\partial x = -\,\partial\kappa.$$

The two groups (a) and (b) are equally numerous, and therefore either can by ascending or descending, allowing for substitutions, exactly replace the other. Now this is the reasoning by which in the ordinary case, when $\kappa = 0$, we prove $\rho = \rho_0\epsilon^{-2hmfx}$. It now proves $\rho = \rho_0\epsilon^{-2hmfx}\epsilon^{-\kappa}$.

I shall refer to this problem later for illustration.

30. The pressure per unit of surface is increased in the ratio $1:(1+\tfrac{1}{2}\kappa)$ as the molecules, from being material points, become spheres with finite diameter c.

But the pressure per unit of surface is the quantity of momentum which is carried through unit of surface in unit of time, Art. 12. Now, so far as this momentum is carried through the surface by molecules *during their free path,* it is not altered in the least by κ acquiring finite value. The increase of the transfer of momentum consists in the case of elastic bodies in the process above explained, namely, the instantaneous transfer of momentum through a finite distance which occurs on collision.

The result of Art. 29 may also be explained thus. The mean effect of all collisions on any sphere is equivalent to a force κf acting from the greater to the less density.

CHAPTER III.

THE DISTRIBUTION OF MOMENTA AMONG THE MOLECULES, ASSUMING CONDITION A.

31. The simplest form of molecule that we can conceive is an elastic sphere, such as described in Arts. 28, 29.

An elastic sphere, so conceived, may be considered as having three degrees of freedom only, namely, motion of translation in space. For the spheres being supposed perfectly smooth, motion of rotation about an axis, if non-existent, will not be produced, and if existing will not be altered, by collisions.

Let u, v, w be the component velocities of a molecule, m its mass. Then the molecules being elastic spheres of mass m, let the number per unit of volume of molecules whose velocities in direction x lie between u and $u+du$ be proportional to $\epsilon^{-hmu^2}du$. This is called Maxwell's distribution. It has been proved by several writers that assuming this distribution to exist, and *assuming condition A* (which is necessary), the distribution will not be disturbed by collisions between the spheres.

My object in the present chapter is not to give another proof of this proposition, but to show in what manner condition A affects the truth, as well as the proof, of the proposition. I shall therefore follow the general method elaborated by Boltzmann and Watson, as being more convenient for my purpose than other known proofs, *e.g.* Professor Tait's.

32. Consider two sets of spheres, one set having mass M, the other mass m. Let the number per unit of volume of M

spheres be ρ_M, of m spheres ρ_m. Let us form a diagram of velocities, the velocity of any sphere of either set being represented in magnitude and direction by a line drawn on the diagram from the origin O to any point P or x, y, z. At P suppose an element of volume $dxdydz$. The number per unit of volume of spheres M whose velocities are represented by lines drawn from O to points within that element shall be

$$\rho_M F(x, y, z)\, dxdydz,$$

or shortly $\rho_M Fdxdydz.$

Call these the class $F(dxdydz)$.

Similarly the number per unit of volume of spheres m whose velocities are represented by lines drawn from O to points within the element of volume $d\xi d\eta d\zeta$ at the point ξ, η, ζ shall be

$$\rho_m f(\xi, \eta, \zeta)\, d\xi d\eta d\zeta,$$

or shortly $\rho_m fd\xi d\eta d\zeta,$

and we will call these the class

$$fd\xi d\eta d\zeta.$$

We may also express the above definitions as follows. The *chance* that a sphere M shall belong at any instant to the class $Fdxdydz$ is $Fdxdydz$. The *chance* that a sphere m shall belong at any instant to the class $fd\xi d\eta d\zeta$ is $fd\xi d\eta d\zeta$.

33. Now assume condition A.

Then the two chances are independent. And therefore the chance that a pair of spheres, M and m, shall belong, M to the class $Fdxdydz$, and m to the class $fd\xi d\eta d\zeta$, is

$$Ffd\xi d\eta d\zeta dxdydz.$$

On our assumption of condition A this is true even if the two spheres are on the point of collision, and therefore very near each other. For that case is not within the exception defined in Art. 17. If we assume B instead of A, it may be true only if the two spheres are at a considerable distance from each other. But in this chapter I assume condition A. On this assumption the number per unit of volume of pairs of spheres, M and m, which have velocities between the limits aforesaid, and for which m lies within the element of volume $d\omega$, so situated that M and m are *approaching collision*, is $Ffd\xi d\eta d\zeta dxdydzd\omega$. If the element $d\omega$ be so situated that M and m are *separating after collision*, the case is within the exception of Art. 17, and therefore condition A does not apply. Let us now define $d\omega$. Let, namely, $R^2 = (x-\xi)^2 + (y-\eta)^2 + (z-\zeta)^2$, so that R is the relative velocity of M and m.

Let c be the sum of their radii. About the centre of M suppose a circular area described with radius c in a plane perpendicular to R, and let

$$d\omega = \pi c^2 R dt.$$

Then the number per unit of volume and time of collisions between spheres M of the class $Fdxdydz$, and spheres m of the class $fd\xi d\eta d\zeta$, is

$$\rho_M \rho_m F dxdydz f d\xi d\eta d\zeta \pi c^2 R.$$

And the whole number per unit of time of collisions which members of the class $Fdxdydz$ undergo with spheres m of any class is

$$\rho_M \rho_m F dxdydz \iiint_{-\infty}^{+\infty} f d\xi d\eta d\zeta \pi c^2 R.$$

Each of these diminishes the number of the class $Fdxdydz$ by one. So the rate of diminution per unit of time of the class $Fdxdydz$ due to collisions between its members and spheres m is

$$\rho_M \rho_m F dxdydz \iiint f d\xi d\eta d\zeta \pi c^2 R \ldots\ldots\ldots\ldots (6).$$

The Effect of Collisions.

34. We have now to find the number of spheres M which by collisions with spheres m pass *into* the class $Fdxdydz$ per unit of volume and time. Let P, p be the centres of M and m.

On a collision the only thing that changes is the direction of R. And that change depends upon (1) the angle ψ which the line of centres Pp at the instant of collision makes with R, (2) the angle ϕ which the plane through a line drawn through the centre of M parallel to R, say Pn, and the point of contact of M and m makes with a fixed plane through Pn.

The direction of R after collision is in the same plane through Pn, and makes the angle 2ψ with Pn. That is the easiest way to picture to ourselves the effect of a collision.

In order that a collision may take place, it is necessary that a line ps drawn through p parallel to R should cut the circular area above mentioned. We may divide that circular area into elements whose type is $2c^2 \sin\psi \cos\psi d\psi d\phi$. Assuming condition A, the line ps is as likely to cut the circular area in any one point as in any other. Therefore the chance that the new direction of R shall make the angle $2\psi \dots 2\psi + d\psi$ with the original direction of R is proportional to $2 \sin\psi \cos\psi d\psi$, that is to $\sin 2\psi d\psi$. It follows that, assuming condition A, for any given direction of R before collision, all directions after collision are equally probable, and on average the whole kinetic energy is divided equally between the spheres.

35. The direction of R after collision is then a function of

$$x, y, z, \xi, \eta, \zeta, \psi, \phi.$$

Let the new values of these variables be denoted by the corresponding accented letters. Evidently ψ, ϕ are unaltered, or

$$\phi' = \phi, \quad \psi' = \psi.$$

All those pairs of spheres for which before collision the variables $x \dots \zeta$ are between

$$x \dots x + dx \dots \zeta \dots \zeta + d\zeta,$$

and ψ, ϕ between limits

$$\psi \dots \psi + d\psi, \quad \phi \dots \phi + d\phi$$

will after collision have these variables between limits denoted by the corresponding accented letters.

Now let $\rho_M F' dx' dy' dz'$ be the number per unit of volume of M spheres which at any instant belong to the class $F' dx' dy' dz'$. Similarly after collision m passes into the class $f' d\xi' d\eta' d\zeta'$, whose numbers are $f' d\xi' d\eta' d\zeta'$.

36. If after collision the velocities of M and m were reversed, without change of their positions, they would by a reverse collision pass into the classes $Fdxdydz$ and $fd\xi d\eta d\zeta$ respectively but with reversed velocities.

It follows that the number of pairs of spheres, M and m, which before collision belong to the classes $F'dx'dy'dz'$ and $f'd\xi'd\eta'd\zeta'$ respectively, and by collision with given values of ψ and ϕ pass into the classes $Fdxdydz$ and $fd\xi d\eta d\zeta$ respectively, is, again assuming condition A,

$$\rho_M\rho_m F'dx'dy'dz'f'd\xi'd\eta'd\zeta'\, 2\sin\psi\cos\psi d\psi d\phi c^2R.$$

37. Now $x', y', z', \xi', \eta', \zeta'$ are functions of $x, y, z, \xi, \eta, \zeta, \psi, \phi$, and of those quantities only. Also the system of two spheres passes with unchanged kinetic energy from one state to the other.

Whence it follows by the general proposition proved later, Art. 50, and can be proved independently, see Watson's *Kinetic Theory of Gases*, second edition, p. 9, that

$$dx'dy'dz'd\xi'd\eta'd\zeta' = dxdydzd\xi d\eta d\zeta \ldots\ldots\ldots\ldots(7).$$

Therefore the number of pairs of spheres, M and m, which per unit of volume and time pass out of the classes $F'dx'dy'dz'$ and $f'd\xi'd\eta'd\zeta'$ into the classes $Fdxdydz$ and $fd\xi d\eta d\zeta$ respectively is with given ψ and ϕ

$$\rho_M\rho_m F'f'dxdydzd\xi d\eta d\zeta\, 2\sin\psi\cos\psi d\psi d\phi c^2R.$$

And if now $\xi, \eta, \zeta, \psi, \phi$ vary, we find for the number of M spheres by which, owing to collisions between M and m, the class $Fdxdydz$ is increased per unit of time the expression

$$\rho_M\rho_m dxdydz \iiint_{-\infty}^{+\infty} d\xi d\eta d\zeta \int_0^{\frac{\pi}{2}}\int_0^{\pi} 2\sin\psi\cos\psi d\psi d\phi F'f'c^2R$$

$$= \rho_M\rho_m dxdydz \iiint d\xi d\eta d\zeta F'f'\pi c^2R.$$

But the number by which the same class is diminished per unit of time by collisions with the m's we found to be

$$\rho_M\rho_m Fdxdydz \iiint fd\xi d\eta d\zeta \pi c^2R.$$

If therefore $\frac{dF}{dt}\,dxdydz$ denote the change per unit of time of $Fdxdydz$, due to collisions of M with m,

$$\frac{dF}{dt}\,dxdydz = dxdydz\iiint d\xi d\eta d\zeta\,(F'f' - Ff)\,\pi c^2 R\;\ldots(8).$$

Similarly

$$\frac{df}{dt}\,d\xi d\eta d\zeta = d\xi d\eta d\zeta\iiint dxdydz\,(F'f' - Ff)\,\pi c^2 R\;\ldots\ldots(8a).$$

38. If $F'f' = Ff$ in all cases in which a pair of spheres M and m can by collision pass from the classes F and f to the classes F' and f' respectively, or *vice versa*, $\frac{dF}{dt} = 0$. Similarly $\frac{df}{dt} = 0$. And this being true for all values of F and f, the motion is stationary. Assuming then condition A, $F'f' = Ff$ is a sufficient condition for stationary motion.

The proof that it is a necessary condition is due to Boltzmann, and is as follows.

Let
$$H = \iiint_{-\infty}^{+\infty} dxdydzF(\log F - 1)$$
$$+\iiint_{-\infty}^{+\infty} d\xi d\eta d\zeta f(\log f - 1).$$

Then
$$\frac{dH}{dt} = \iiint dxdydz\,\frac{dF}{dt}\log F$$
$$+\iiint d\xi d\eta d\zeta\,\frac{df}{dt}\log f.$$

And substituting for $\frac{dF}{dt}$ and $\frac{df}{dt}$ their values above found,

$$\frac{dH}{dt} = \iiint_{-\infty}^{+\infty} dxdydz\iiint_{-\infty}^{+\infty} d\xi d\eta d\zeta \iint (F'f' - Ff)(\log F + \log f)\,\pi c^2 R$$
$$= \iiint dxdydz\iiint d\xi d\eta d\zeta\,(F'f' - Ff)\log(Ff)\,\pi c^2 R\ldots(9).$$

But in the course of this integration x, y, z and ξ, η, ζ assum all possible positions on the diagram of velocities, and therefo assume the positions corresponding to any F' and f', and there fore F and f among other values assume the values F' and f Whence

$$\frac{dH}{dt} = \iiint dxdydz \iiint d\xi d\eta d\zeta\,(Ff - F'f')\log F'f'\pi c^2 R\ldots(10).$$

and adding together (9) and (10)

$$\frac{dH}{dt} = \tfrac{1}{2}\iiint dxdydz \iiint d\xi d\eta d\zeta\,(F'f' - Ff)\log \frac{Ff}{F'f'}\,\pi c^2 R\ldots(11$$

And this is necessarily negative, if not zero, and then onl zero when $F'f' = Ff$ for every case in which two spheres ca pass by collision from the classes F and f to the classes F' an f' respectively, or *vice versa*. But in stationary motion $\frac{dH}{dt}$ must be zero. Therefore in stationary motion, given conditio A, $F'f' = Ff$, is a necessary condition. A distribution o velocities in which $F'f' = Ff$ for all cases in which a pair o spheres can pass by collision from the state F and f to th state F' and f' or *vice versa* shall be called the *normal distribution.* Any other distribution shall be called *an abnorma distribution.* The H theorem proves that when the distributio is abnormal $\frac{dH}{dt}$ is negative.

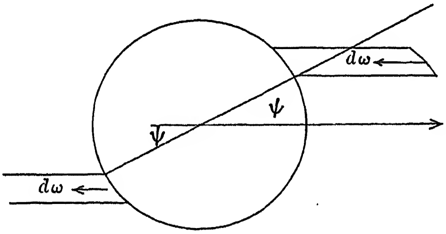
This is known as Boltzmann's minimum theorem, or the H theorem, and H is *Boltzmann's minimum function,* or, as he sometimes calls it, the *Entropy function.* The theorem is as here given, founded on, and depends for its existence upon condition A, without which we cannot use the product Ff to express the frequency, or chance, of the simultaneous occurrence in collisions of the two states denoted by f and F.

On the H theorem. An objection considered.

39. If when the entire system of elastic spheres has, with H diminishing, reached a certain state, all the velocities were simultaneously reversed without change of the coordinates, the system would exactly retrace its course with H increasing. It is therefore possible, when a system is set in motion, for H to increase in that motion. This was at one time considered an objection to the theorem, because the theorem was supposed to prove that *under no possible circumstances* could H increase. It however does not profess to prove that H always diminishes, but that, *assuming a certain condition* H must diminish on average. For the assumption underlies the whole proof as hitherto given.

Now to meet this objection, consider two spheres, M having velocities x, y, z, and m having ξ, η, ζ. Construct a spherical surface of radius c about the centre of M, and consider the element of volume

$$2c^2 \sin\psi \cos\psi \, d\psi \, d\phi \, R dt = d\omega.$$



If m be within $d\omega$, the two spheres are either (1) approaching collision, or (2) separating after collision, according as $d\omega$ is on one or the other side of M. Condition A asserts that the number per unit of volume of pairs of spheres, M and m, belonging respectively to the classes F and f, which are *approaching* a collision of that kind—*i.e.* a collision with the given ψ and ϕ—is $Ffdx \ldots d\zeta d\omega$, see Art. 17 and note. But condition A does not assert that the number per unit of volume of such pairs which are *separating after* a collision of that kind is $Ffdx \ldots d\zeta d\omega$, because that case is within the exception of Art. 17. In fact if x, y, z and ξ, η, ζ denote the precollision velocities of the separating pairs, x', y', &c. their velocities after collision, the separating pairs are the identical pairs which dt seconds ago had respectively velocities

$$x \ldots x + dx \ldots\ldots \zeta \ldots \zeta + d\zeta,$$

and were approaching a collision of the kind in question. The number per unit of volume of the separating pairs is therefore by our assumption of condition A

$$Ff,\ dx\ldots d\zeta,\ d\omega,$$

or which is the same thing,

$$Ffdx',\ldots d\zeta' d\omega,$$

and not $F'f'dx'\ldots d\zeta' d\omega$. (We are assuming at present that $Ff \neq F'f'$.) Now in the reversed course the pairs which in the original course were separating have become the approaching pairs, and *vice versa*. Therefore in the reversed course the number per unit of volume of pairs, M and m, which, belonging respectively to the classes F' and f', are approaching a collision of the kind in question, is $Ffdx'\ldots d\zeta' d\omega$, and not $F'f'dx'\ldots d\zeta' d\omega$, as according to condition A it should be. We see then that condition A is not satisfied in the reversed motion, and why not.

The fact then that in the reversed motion H increases with the time is no objection to the H theorem as a mathematical proposition, because the reversed motion does not satisfy the condition on which the H theorem is based.

40. We now see the necessity for the exception referred to in Art. 17. For if condition A continues to exist throughout the direct motion without that exception, it must also continue to exist throughout the reversed motion. Therefore by the H theorem $\frac{dH}{dt}$ is negative or zero in both motions. But if it be negative, and differ from zero, in one of those motions, it must be positive in the other. Therefore $\frac{dH}{dt}$ must, if we assume condition A without exception, be zero in both motions.

In other words, if we assume condition A with the exception, the mathematical consequence of our assumption is that H is either minimum or diminishing, as the theorem asserts. If we assume condition A without the exception, the mathematical consequence of our assumption is that H is minimum already. This condition is satisfied by Maxwell's distribution.

41. We must now consider Boltzmann's own assumption that the motion is "molecular-ungeordnet." It being assumed that in the direct course the motion is molecular-ungeordnet, is it molecular-ungeordnet in the reverse course, or not? I think Boltzmann's answer to this question would be in the negative, on the ground that we, or Maxwell's corps of demons, have "ordered" (geordnet) the motion by the very act of reversal. If this be so, then "molecular-ungeordnet" has, as applied to this theorem, precisely the same properties as my condition A. See *Vorlesungen*, p. 42.

Let us endeavour to construct synthetically a system which shall without doubt be molecular-ungeordnet. The molecules being distinguished by numbers, I ask (say) Dr Watson to assign velocities to them according to any law he pleases. Then I, in complete ignorance of those assigned velocities, scatter the molecules at haphazard through space, and they shall start from the positions which I so give them with the velocities so assigned by Dr Watson. That is, *primâ facie*, a molecular-ungeordnet system—in fact it is as near an approach to chaos as is possible in an imperfect world.

Clearly also in this system condition A is satisfied, and the system will, or in all probability will, move from its initial position with H diminishing. Equally clear is it that if in the initial position all the velocities were reversed, condition A would be satisfied, and the system would, or in all probability would, move off in the opposite direction with H diminishing*. It follows then that if the selected distribution of velocities be abnormal, the state in which we have placed the system is one *from* which the system can and probably will move with H diminishing, but *into* which it must move with H increasing.

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* This statement is not inconsistent with that of Arts. 39 and 40 that $\frac{dH}{dt}$ changes sign on reversal of the velocities. For in those articles the pairs of molecules having velocities x', ξ', &c. are separating after an actual collision, before which they had velocities x, ξ, &c. Corresponding to the classes x, ξ, their number is Ff. In the synthetic system no collision has taken place, and the number is $F'f'$.

If the system were to move through that state, $\frac{dH}{dt}$ would be discontinuous.

It may indeed, if the distribution of velocities happens to be the normal one, be *in* Maxwell's distribution. It cannot be one of a series of states through which the system passes in its approach to Maxwell's distribution, as the H theorem requires. The system then which I have supposed to be constructed is not, as appears to me, in Boltzmann's sense molecular-ungeordnet. It should seem that the molecular ungeordnet state must cease to be such on reversal of the velocities.

What the H theorem proves then is this, that the distribution of velocities expressed by the equation $F'f' = Ff$ is the only distribution which can be permanent consistently with the existence, and the continued existence, of condition A or its equivalent. It is assumed without proof, and as I hope to show in the succeeding chapters is not generally true, that condition A can and does continue to exist.

The rate at which H diminishes has been calculated by Tait, Watson, and others for certain very interesting cases. See Watson's work above referred to, Art. 15.

42. Boltzmann (see *Berlin Sitzungsberichte*, February 1897) considers that we have in this behaviour of the system a true irreversible process. That term is generally applied only to processes involving dissipation of energy, that is conversion of some other form of energy into heat. If however heat, or temperature is to be explained as the kinetic energy of molecules or atoms moving according to usual dynamical laws, every process, even if it does involve conversion of other forms of energy into heat, is theoretically reversible; would in fact be reversed if at any instant all the velocities were reversed, as we assumed them to be in discussing the H theorem. If that be so, by asserting that any process is irreversible we assert only that by no means within our power can we reverse it, because, that is, we cannot control individual molecules. It is in this sense that, as I understand, the diminution of H in accordance with the theorem would be called by Boltzmann an irreversible process.

Boltzmann also shows (*Vorlesungen*, pp. 58—60) that $-H$ differs by a constant only from the logarithm of the chance of the system being in its actual state, and therefore as H diminishes in absolute value, the system passes from a less to a more probable state. See note at end of chapter.

43. A solution of the equation

$$F'f' = Ff,$$

for the two sets of elastic spheres is

$$\left.\begin{aligned} F &= \left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \epsilon^{-hM(x^2+y^2+z^2)} \\ f &= \left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \epsilon^{-hm(\xi^2+\eta^2+\zeta^2)} \end{aligned}\right\} \ldots\ldots\ldots\ldots\ldots (12).$$

That is found by treating the kinetic energy as the only thing which remains unchanged by the collision. It follows from this solution that for the same sphere $\overline{x^2} = y^2 = z^2$, and that for different spheres $M\overline{x^2} = m\xi^2$ &c., or the mean kinetic energy is the same for each sphere whatever its mass.

44. The complete solution of the equation $Ff = F'f'$, as given by Boltzmann, *Vorlesungen*, p. 131, is

$$f = A\epsilon^{-hQ},$$

where A is a function of the coordinates, and

$$Q = m\{(\alpha - u)^2 + (\beta - v)^2 + (\gamma - w)^2\} \ldots\ldots\ldots\ldots (13),$$

u, v, w being constant velocities; F has the corresponding value.

In stationary motion $\dfrac{df}{dt} = 0$, that is

$$\left\{(\alpha - u)\frac{d}{dx} + \text{\&c.} + \frac{d\alpha}{dt}\frac{d}{d\alpha} - \frac{du}{dt}\frac{d}{du} + \text{\&c.}\right\} A\epsilon^{-hQ} = 0.$$

Suppose now the system to be in a field of external force whose potential is χ, *e.g.* the column of Art. 29.

If no other forces act on the system than those derived from χ, we have

$$m\left(\frac{d\alpha}{dt}-\frac{du}{dt}\right)=-\frac{d\chi}{dx} \quad\text{....................(14)},$$

and therefore the equation becomes

$$(\alpha-u)\left(\frac{dA}{dx}+2hA\,\frac{d\chi}{dx}\right)\epsilon^{-hQ}+\text{\&c.}=0 \quad\text{........(15)},$$

the solution of which is $$A=\epsilon^{-2h\chi} \quad\text{....................(16)}.$$

For instance, if the molecules be elastic spheres of infinitely small diameter, or material points, between which no collisions occur, there are no forces except those derived from χ, and we deduce by the above method, $A=\epsilon^{-2h\chi}$.

The expression now asserts that the chance of a molecule having velocities $\alpha\ldots\alpha+d\alpha$ &c., and being in a position where the potential of the external force is $\chi\ldots\chi+d\chi$, is

$$\epsilon^{-2h\chi}\,\epsilon^{-hm\{(\alpha-u)^2+\text{\&c.}\}}\,d\alpha\,d\beta\,d\gamma\,d\chi.$$

It follows that the distribution of the velocities is the same for all values of χ, that is in all parts of the system, and that the number of molecules per unit of volume is proportional to $\epsilon^{-2h\chi}$. This agrees with the result of Art. 29, because in the case now supposed $\kappa=0$.

45. If the spheres have finite diameter c, so that collisions do occur, there *are* other forces acting besides those derived from χ, namely, the infinite forces assumed to act for infinitely short times during collisions. And it is no longer true that

$$m\frac{d}{dt}(\alpha-u)=-\frac{d\chi}{dx},$$

and we cannot obtain the result

$$f=\epsilon^{-2h\chi}\,\epsilon^{-hm\{(\alpha-u)^2+\text{\&c.}\}},$$

except by ignoring the infinite forces altogether. It is true indeed that they act in equal and opposite pairs, but no solution can be satisfactory which takes no account of them. See further as to this problem *post*, Art. 103.

46. If the intermolecular forces are finite, and have a potential ψ, we have

$$m\frac{d}{dt}(\alpha - u) = -\frac{d\chi}{dx} - \frac{d\psi}{dx}.$$

And our formula leads to the conclusion that

$$A = \epsilon^{-2h(\chi+\psi)} \quad \text{.....................(17)},$$

expressing now the fact that as before the distribution of velocities is on an average the same for any molecule, in whatever position it happens to be, not only with respect to the external field, but also with respect to other molecules—but that the number of molecules per unit of volume in a position in which the whole potential is $\chi + \psi$ is on average $\epsilon^{-2h(\chi+\psi)}$. I see no reason why we should hesitate to accept this result, or how we can avoid accepting it, except that Dr Watson (in the work above referred to, pp. 70, 71) hesitates to accept it, though I do not understand him to deny its validity. He puts the case that, with finite intermolecular forces, a molecule P may have a sphere of action, within which may be many other molecules. Any individual molecule outside of the sphere of action exerts on P a force which is negligible. But the infinite number of molecules outside of the sphere of action may exert on P a sensible force. And he shows that this may be included in the fixed centre forces. But he refrains from drawing any conclusion for the molecules within the sphere of action.

Boltzmann and Watson's generalisation.

47. Our molecules regarded as elastic spheres have each only three degrees of freedom, that namely of motion of translation.

Let us now attribute to our molecules the most general form possible.

Let a molecule m be a material system, whose position and state at any instant are defined by n generalised coordinates $q_1 \ldots q_n$, and the corresponding momenta $p_1 \ldots p_n$.

Let ρ_m be the number of molecules of the kind m per unit of volume.

Let $$\rho_m f(q_1 \dots q_n p_1 \dots p_n)\, dq_1 \dots dp_n,$$

or shortly $$\rho_m f dq_1 \dots dp_n,$$

denote the number per unit of volume of molecules m for which the variables lie between the limits

$$\left.\begin{array}{l} q_1 \dots q_1 + dq_1 \\ \dots\dots\dots\dots\dots \\ q_n \dots q_n + dq_n \\ p_1 \dots p_1 + dp_1 \\ \dots\dots\dots\dots\dots \\ p_n \dots p_n + dp_n \end{array}\right\} \dots\dots\dots\dots\dots\dots\dots\dots (c),$$

or, as we shall express it, are in the state c.

We may express this in a different way that *the chance* of an m molecule being in the state c is $f dq_1 \dots dp_n$.

It is assumed that the molecule is, so far as its own internal forces are concerned, stable. That is that if it be now in the state c, and if no forces except its own internal forces act upon it, it will after the lapse of some time, greater or less, find itself in the state (c) again, except so far as the coordinates defining its position in space, which are included in $q_1 \dots q_n$, are changed by its motion of translation. It is also assumed that f will not be altered by reversing the sign of $p_1 \dots p_n$ simultaneously. And therefore f cannot contain odd powers or products of the p's.

In the same region let there be another set of molecules M, each having r degrees of freedom, whose coordinates and momenta are denoted respectively by $Q_1 \dots Q_r$ and $P_1 \dots P_r$. And about these make the same assumption as above stated.

Let ρ_M be the number of M molecules per unit of volume.

Let $$\rho_M F(Q_1 \dots Q_r P_1 \dots P_r)\, dQ_1 \dots dP_r,$$

or shortly $$\rho_M F dQ_1 \dots dP_r,$$

denote the number per unit of volume of molecules M for which the same variables lie between the limits

$$\left.\begin{array}{l} Q_1 \ldots Q_1 + dQ_1 \\ \ldots\ldots\ldots\ldots\ldots \\ Q_r \ldots Q_r + dQ_r \\ P_1 \ldots P_1 + dP_1 \\ \ldots\ldots\ldots\ldots\ldots \\ P_r \ldots P_r + dP_r \end{array}\right\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(C)},$$

or, as we may express it, are in the state C.

48. Let $\phi(q_1 \ldots q_n\, Q_1 \ldots Q_r)$ be a function of the coordinates of two molecules m and M, such that when ϕ is positive there is no mutual action between the two molecules.

Let us now make an assumption equivalent, with respect to the molecules now under consideration, to condition A. Let us assume namely that so long as ϕ is positive and $\frac{d\phi}{dt}$ negative, the two chances F and f are independent. And therefore the number per unit of volume of pairs of molecules, one belonging to the m's and the other to the M's, for which at any instant the variables lie, for m within the limits c, and for M within the limits C, is

$$\rho_m \rho_M F f dq_1 \ldots dp_n dQ_1 \ldots dP_r.$$

When ϕ passes through zero the two molecules pass into their *sphere of mutual action*, and an *encounter* commences between them. The chances F and f generally cease to be independent.

It may be the case that ϕ, having become negative, would if the two molecules are not influenced from without, remain negative for all time. The two molecules, that is, may, each remaining stable, form a permanent union revolving round one another in a closed orbit. I shall not consider that case, but assume that after a certain time τ, ϕ will again pass through zero and become positive. The encounter ceases when ϕ again becomes zero. All those pairs of molecules for which at a given instant ϕ lies between zero and $\frac{d\phi}{dt}dt$, $\frac{d\phi}{dt}$ being positive, will within the time dt after that instant commence, and as I am now assuming, will in due time afterwards complete, an encounter. The number per unit of volume and time of such encounters must therefore contain the factor $\frac{d\phi}{dt}$.

49. But the two molecules have between them only $n+r$ degrees of freedom. We must therefore use ϕ for one of the generalised coordinates defining the position of the double system.

Let us substitute ϕ for q_n. Then all those pairs of molecules, m and M, for which at any instant the variables other than q_n lie within the limits c and C respectively, and for which at the same instant ϕ lies between zero and $\frac{d\phi}{dt}dt$, will in the interval of time dt after that instant encounter one another. The number of such encounters which commence in time dt is therefore

$$\rho_m \rho_M F f dq_1 \dots dq_{n-1} dp_1 \dots dp_n dQ_1 \dots dP_r \frac{d\phi}{dt} dt.$$

As a consequence of the encounter, after the time τ the variables will be found between the limits

$$\left.\begin{array}{l} q_1' \cdots\cdots\cdots q_1' + dq_1' \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ q'_{n-1} \cdots q'_{n-1} + dq'_{n-1} \\ p_1' \cdots\cdots\cdots p_1' + dp_1' \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ p_n' \cdots\cdots p_n' + dp_n' \end{array}\right\} \cdots\cdots\cdots\cdots\cdots\cdots (c')$$

for m, and

$$\left.\begin{array}{l} Q_1' \cdots Q_1' + dQ_1' \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ P_r' \cdots P_r' + dP_r' \end{array}\right\} \cdots\cdots\cdots\cdots\cdots\cdots (C')$$

for M, and ϕ between zero and $\frac{d\phi'}{dt}dt$, and the encounter ceases as ϕ again passes through zero. The pair of molecules pass out of their sphere of mutual action.

According to our notation the number per unit of volume of pairs of molecules, m and M, for which the variables lie between these limits c′, C′, with $\frac{d\phi}{dt}$ positive, is

$$\rho_m \rho_M F'f' dq_1' \ldots dq'_{n-1} dp_1' \ldots dp_n' dQ_1' \ldots dP_r' \frac{d\phi'}{dt} dt.$$

Conversely if at the beginning of the time τ the variables were in the limits c′, C′, ϕ', $\frac{d\phi'}{dt}\,dt$ with reversed velocities, they would at the end of the same time τ be found within the limits c, C with reversed velocities. We may call these reversed encounters. The number of reversed encounters less the number of direct encounters per unit of volume and time is

$$\rho_m \rho_M F'f' dq_1' \ldots dq'_{n-1} dp_1' \ldots dp_n' dQ_1' \ldots dP_r' \frac{d\phi'}{dt} dt$$
$$- \rho_m \rho_M F f dq_1 \ldots dq_{n-1} dp_1 \ldots dp_n dQ_1 \ldots dP_r \frac{d\phi}{dt} dt.$$

50. It can now be proved (the system being conservative) that

$$dq_1' \ldots dq'_{n-1} dp_1' \ldots dp_n' dQ_1' \ldots dP_r' \frac{d\phi'}{dt}$$
$$= dq_1 \ldots dq_{n-1} dp_1 \ldots dp_n dQ_1 \ldots dP_r \frac{d\phi}{dt}.$$

For the accented variables q_1', &c. are all functions of the unaccented variables and of the time τ. And as τ is the same for every system within the initial limits, we have

$$\frac{dS}{dq_1'} = p_1', \quad \frac{dS}{dq_2'} = p_2', \text{ \&c.},$$

where S is Hamilton's Principal function for the motion in question. Similarly

$$\frac{dS}{dq_1} = -p_1, \quad \frac{dS}{dq_2} = -p_2, \text{ \&c.}$$

Now writing $d\phi$ for $\frac{d\phi}{dt}\,dt$ and $d\phi'$ for $\frac{d\phi'}{dt}\,dt$,

$$\begin{aligned}
&dq_1' \dots dq'_{n-1}\, d\phi'\, dp_1' \dots dp_n'\, dQ_1' \dots dP_r' \\
&\quad = dq_1' \dots dq'_{n-1}\, d\phi'\, dQ_1' \dots dQ_r' \times dp_1' \dots dp_n'\, dP_1' \dots dP_r' \\
&\quad = dq_1' \dots dq'_{n-1}\, d\phi'\, dQ_1' \dots dQ_r'\, dq_1 \dots dq_{n-1}\, d\phi\, dQ_1 \dots dQ_r \\
&\qquad \times \Sigma \pm \frac{dp_1'}{dq_1}\,\frac{dp_2'}{dq_2} \dots \frac{dP_r'}{dQ_r},
\end{aligned}$$

where the last factor denotes the functional determinant

$$\begin{array}{llll}
\frac{dp_1'}{dq_1} & \frac{dp_1'}{dq_2} & \dots & \frac{dp_1'}{d\phi}, \\
\frac{dp_2'}{dq_1} & \multicolumn{3}{l}{\dots\dots\dots\dots\dots}
\end{array}$$

and since

$$p_1' = \frac{dS}{dq_1'},\quad \frac{dp_1'}{dq_1} = \frac{d^2S}{dq_1 dq_1'},\ \text{\&c.},$$

the functional determinant may be written

$$\begin{array}{llll}
\frac{d^2S}{dq_1 dq_1'} & \frac{d^2S}{dq_1' dq_2} & \dots & \frac{d^2S}{dq_1' d\phi}, \\
\frac{d^2S}{dq_1 dq_2'} & \multicolumn{3}{l}{\dots\dots\dots\dots\dots\dots\dots} \\
\multicolumn{4}{l}{\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots}
\end{array}$$

In the same way

$$\begin{aligned}
&dq_1 \dots dq_{n-1}\, d\phi\, dp_1 \dots dp_n\, dQ_1 \dots dP_r \\
&\quad = dq_1 \dots dq_{n-1}\, d\phi\, dQ_1 \dots dQ_r \times dq_1' \dots dq'_{n-1}\, d\phi'\, dQ_1' \dots dQ_r' \\
&\qquad \times \Sigma \pm \frac{dp_1}{dq_1'}\,\frac{dp_1}{dq_2'} \dots,
\end{aligned}$$

and the functional determinant has, but for its sign, the same value as before. Hence the continued products of the differentials are numerically equal, that is

$$\begin{aligned}
&dq_1' \dots dq'_{n-1}\, d\phi'\, dp_1' \dots dp_n'\, dQ_1' \dots dP_r' \\
&\quad = dq_1 \dots dq_{n-1}\, d\phi\, dp_1 \dots dp_n\, dQ_1 \dots dP_r \quad \dots\dots(18),
\end{aligned}$$

and therefore the excess of the reverse over the direct encounters per unit of volume and time is

$$\rho_M\rho_m(F'f'-Ff)\,dq_1\ldots dq_{n-1}d\phi dp_1\ldots dp_n\times dQ_1\ldots dP_r,$$

or

$$\frac{dF}{dt}=\rho_M\rho_m\,dQ_1\ldots dP_r\iiint(F'f'-Ff)\,dq_1\ldots dq_{n-1}d\phi dp_1\ldots dp_n\,;$$

and is zero if in all cases $F'f'=Ff.$

A corresponding equation holds for $\frac{df}{dt}$. See further for this proposition Watson's *Kinetic Theory of Gases*, second edition, Arts. 8, 10, 12, 13.

51. As this property is true for all values of F and f with the corresponding F' and f', we see that if $F'f'=Ff$ in all cases where a pair of molecules can by encounter pass out of the classes F, f into the classes F', f' respectively, or *vice versa*, we have a *sufficient condition* for stationary motion.

The H theorem of Art. 38 can easily be adapted to prove that it is also a necessary condition. Further we may take for solution of the equation $F'f'=Ff$,

$$F=Ce^{-2hT},\quad f=C'e^{-2hT'},$$

where T is the kinetic energy of the molecule M, and T' that of m; and if T, T' can be reduced to the sum of squares of the velocities, we get a result analogous to that obtained for elastic spheres in Art. 43, namely that, as a consequence of condition A, the mean kinetic energy is the same for each degree of freedom.

52. It is necessary here to point out what further assumptions, besides condition A, we have made concerning our molecules in the above demonstration. We expressly assumed in Art. 47, that each molecule left to itself is *stable*, that is, that so far as the mutual forces between its parts are concerned, the coordinates and momenta, whatever values they have at this instant, will or may, at some future time pass simultaneously through the same values or infinitely near to them, the coordinates x, y, z defining the position in space of the centre of inertia being excepted. We also expressly assumed that if two molecules pass into an encounter, they pass out of it again, that is do not form a permanent union. We have further assumed tacitly that each molecule is stable, not only under the influence of its own internal forces, but also under the influence of the new forces which may be developed during its encounter with another molecule. Suppose for instance for an m molecule $f = \epsilon^{-hs}$, where s is a quadratic function of the momenta $p_1 \ldots p_n$ with coëfficient functions of $q_1 \ldots q_n$. A necessary condition of stability is then that s shall be positive for all possible values of the p's. And that requires that the determinant of the coefficients in s, which we will call d, and all its coaxial minors, shall be positive. See Appendix (q).

If $$s = a_1 \frac{p_1^2}{2} + b_{12} p_1 p_2 + \&c.,$$

then $$d = \begin{vmatrix} a_1 & b_{12} & b_{13} \\ b_{12} & a_2 & b_{23} \\ \ldots & \ldots & \ldots \end{vmatrix}.$$

Similarly in order that an M molecule shall be stable if left to itself, we have if

$$F = \epsilon^{-hS}, \text{ and } S = A_1 \frac{P_1^2}{2} + B_{12} P_1 P_2 + \&c.,$$

$$D = \begin{vmatrix} A_1 & B_{12} & B_{13} \\ B_{12} & A_2 & B_{23} \\ \ldots & \ldots & \ldots \end{vmatrix};$$

and D must be positive. And so long as the two molecules do not influence each other, the condition is that Dd shall be positive, which is necessarily true if it is true for d and D separately. But when the two molecules are within the sphere of their mutual action, the corresponding criterion of stability is that $s + S$ shall be positive whatever values the velocities may have. If Δ be the determinant of the coefficients in $S + s$, Δ, and all its coaxial minors must be positive.

But if we form the determinant Δ for the coefficients in $s+S$, it will generally during an encounter or when $\phi<0$ contain constituents of the form pP. The condition may fail for Δ, although it held when $\phi>0$ for d and D separately. So that the two molecules, though stable separately, may be unstable together. The encounter may be the death of the molecule.

Note on the H Theorem, Art. 42.

The H Theorem proves strictly that, assuming the independence of the chances (Art. 17), $\frac{dH}{dt}$ is generally negative. It is claimed for it, as a physical theorem, that the diminution of H is analogous to the increase of Entropy in irreversible processes. To make that analogy complete, the chance of $\frac{dH}{dt}$ being positive ought to diminish indefinitely as time increases. I will state the difficulties that this view presents to me, without saying that they are insuperable.

A finite number of molecules in a finite space are set in motion at an initial epoch at random, in the manner described in Art. 41, and then left for infinite time, undisturbed from without, under conservative forces. Initially $\frac{dH}{dt}$ is almost certainly negative. After time t the coordinates and momenta of every molecule are determinate functions of t and of all the initial coordinates and momenta. If C, C' be two successive states of the system, each in its turn a consequence of the same initial state, in what sense is C less probable than C'? It may be that the initial state, formed as we have formed it, is less likely to be C than C'. But the chance of state C at time t is not proportional to the chance of the initial state being C. It is then improbable that the initial state should be one in which $\frac{dH}{dt}$ is positive. It is not proved to be improbable that it should be one, a necessary consequence of which is that $\frac{dH}{dt}$ will be positive at time t.

Again, the continued independence of the chances, if conceded, attributes to every subsequent state of the system the same properties as the initial state has, which would be right if the system were continually receiving external disturbances. Can it be conceded for the isolated system? Let S be the Principal function, x, x' type coordinates of two molecules at time t. If $x=x'$ nearly, are the momenta $\frac{dS}{dx}$, $\frac{dS}{dx'}$, correlated or independent? I think it can be proved that they are correlated. If so, the formula 8 of Art. 37, expressing $\frac{dF}{dt}$, is inexact. And the theorem fails to prove $\frac{dH}{dt}$ negative, except when the factors $F'f'-Ff$ are great, that is when H deviates widely from its normal value.

CHAPTER IV.

CORRELATION OF VELOCITIES. FINITE FORCES.

53. I PROPOSE to prove in this and the next chapter that in a system consisting of molecules of finite dimensions in stationary motion, it is not true for molecules very near to one another, that the chances of their having velocities between assigned limits are independent, as condition A assumes: but on the contrary if the forces be repulsive, they tend to move on average in the same direction; and therefore that in dealing with their encounters, or (in the case of rigid bodies) their collisions, we cannot legitimately base our conclusions on condition A, except in the limiting case when the density—*i.e.* the ratio which the aggregate volume of all the molecules in unit of volume bears to unit of volume,—is infinitely small, though conclusions based on condition A are approximately accurate for gases under ordinary conditions.

In the present chapter I shall deal only with the case of finite intermolecular forces.

Let m, &c. be the masses of a number of molecules in stationary motion. Let x, y, z denote the coordinates of m, x', y', z' those of any other molecule as m'. Let r be the distance from m to m'. Let f be a function of r which is everywhere positive, finite and continuous, which is of negative degree except for very small values of r, and such that $\int_0^\infty 4\pi r^2 f dr$ is finite.

Then for any m, Σf is the sum of the values of f, referred to the position of m as centre, for all the other molecules;

and if ρ be the number of molecules per unit of volume, $\Sigma f = \int_0^\infty 4\pi r^2 \rho f dr$. Also $\Sigma r \frac{df}{dr}$ has corresponding meaning.

Extension of Clausius' Theorem.

54. We can now put the Clausian equation in a modified form as follows,

$$\frac{d}{dt}\left\{\Sigma m\left(x\frac{dx}{dt} + y\frac{dy}{dt} + z\frac{dz}{dt}\right)\Sigma f\right\} = 0 \,\ldots\ldots\ldots\, \text{(I)},$$

for the function within brackets has a determinate value at every instant, and cannot on average increase or diminish with the time, the motion being stationary.

Again for the same reason,

$$\frac{d}{dt}\left\{\Sigma m\frac{dx}{dt}\Sigma fx' + \Sigma m\frac{dy}{dt}\Sigma fy' + \Sigma m\frac{dz}{dt}\Sigma fz'\right\} = 0 \ldots \text{(II)}.$$

Here the first Σ denotes that every molecule successively is to play the part of m, and the second Σ includes all the molecules except m each with its own x', y', z', and each with its own f referred to the position of m for the time being.

Subtracting I. from II. we obtain

$$\Sigma m\frac{dx}{dt}\Sigma f\frac{dx'}{dt} + \Sigma m\frac{dy}{dt}\Sigma f\frac{dy'}{dt} + \Sigma m\frac{dz}{dt}\Sigma f\frac{dz'}{dt}$$

$$-\Sigma m\left\{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right\}\Sigma f$$

$$+\Sigma m\frac{d^2x}{dt^2}\Sigma f(x'-x) + \Sigma m\frac{d^2y}{dt^2}\Sigma f(y'-y) + \Sigma m\frac{d^2z}{dt^2}\Sigma f(z'-z)$$

$$+\Sigma m\frac{dx}{dt}\Sigma(x'-x)\frac{df}{dt} + \Sigma m\frac{dy}{dt}\Sigma(y'-y)\frac{df}{dt}$$

$$+\Sigma m\frac{dz}{dt}\Sigma(z'-z)\frac{df}{dt} = 0 \,\ldots\ldots\ldots\, \text{(III)}.$$

Again, $$\frac{df}{dt} = \frac{df}{dr}\frac{dr}{dt}.$$

And if λ, μ, ν be the direction cosines of mm', or r, drawn from m to m', $x'-x=\lambda r$ &c., and

$$\frac{dr}{dt}=\lambda\frac{dx'}{dt}+\mu\frac{dy'}{dt}+\nu\frac{dz'}{dt}$$
$$-\left(\lambda\frac{dx}{dt}+\mu\frac{dy}{dt}+\nu\frac{dz}{dt}\right),$$

and the last line of III. becomes

$$\Sigma m\Sigma r\frac{df}{dr}\left(\lambda\frac{dx}{dt}+\mu\frac{dy}{dt}+\nu\frac{dz}{dt}\right)\left(\lambda\frac{dx'}{dt}+\mu\frac{dy'}{dt}+\nu\frac{dz'}{dt}\right)$$
$$-\Sigma m\Sigma r\frac{df}{dr}\left(\lambda\frac{dx}{dt}+\mu\frac{dy}{dt}+\nu\frac{dz}{dt}\right)^2.$$

That is, since $\lambda\mu=\lambda\nu=\mu\nu=0$ on average, and

$$\lambda^2=\mu^2=\nu^2=\frac{1}{3}$$

on average, the last line of III. becomes,

$$\Sigma m\Sigma r\frac{df}{dr}\left(\lambda\frac{dx}{dt}+\mu\frac{dy}{dt}+\nu\frac{dz}{dt}\right)\left(\lambda\frac{dx'}{dt}+\mu\frac{dy'}{dt}+\nu\frac{dz'}{dt}\right)$$
$$-\frac{1}{3}\Sigma m\Sigma r\frac{df}{dr}\left\{\left(\frac{dx}{dt}\right)^2+\left(\frac{dy}{dt}\right)^2+\left(\frac{dz}{dt}\right)^2\right\}.$$

Again, $$-\frac{1}{3}\Sigma r\frac{df}{dr}=-\frac{1}{3}\int_0^\infty 4\pi r^2\rho r\frac{df}{dr}\,dr$$

$$=\left|-\frac{1}{3}4\pi r^3\rho f\right|_{r=0}^{r=\infty}+\int 4\pi r^2\rho f dr+\int\frac{4}{3}\pi r^3 f\frac{d\rho}{dr}\,dr$$

$=\Sigma f$ by the conditions for f, if $\frac{d\rho}{dr}=0$.*

Again, $$m\frac{d^2x}{dt^2}=X,\ \&c.$$

if X, Y, Z be the components of all the forces, whether external or intermolecular, acting on m.

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* If the molecules be scattered uniformly $\frac{d\rho}{dr}=0$ on average. If not uniformly, it will be generally negative, because we take a molecule for centre, and there are more molecules where ρ is greater. But (see Art. 106) it will be small. If negative it helps my present argument, but I shall treat it as zero.

Therefore $$m\frac{d^2x}{dt^2}\Sigma f\,\overline{x'-x} = X\Sigma f(x'-x),$$

$$m\frac{d^2y}{dt^2}\Sigma f\,\overline{y'-y} = Y\Sigma f(y'-y),$$

$$m\frac{d^2z}{dt^2}\Sigma f\,\overline{z'-z} = Z\Sigma f(z'-z).$$

Making these substitutions, and arranging the terms, we find

$$\frac{d}{dt}\left\{\Sigma m\frac{dx}{dt}\Sigma f(x'-x) + \&\text{c.}\right\} = 0$$

$$= -\Sigma f\Sigma m\left\{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right\}$$

$$+ \Sigma m\Sigma f\left(\frac{dx}{dt}\frac{dx'}{dt} + \frac{dy}{dt}\frac{dy'}{dt} + \frac{dz}{dt}\frac{dz'}{dt}\right)$$

$$+ \Sigma X\Sigma f(x'-x) + \Sigma Y\Sigma f(y'-y) + \Sigma Z\Sigma f(z'-z)$$

$$+ \Sigma m\Sigma r\frac{df}{dr}\left(\lambda\frac{dx}{dt} + \mu\frac{dy}{dt} + \nu\frac{dz}{dt}\right)\left(\lambda\frac{dx'}{dt} + \mu\frac{dy'}{dt} + \nu\frac{dz'}{dt}\right)$$

$$+ \Sigma f\Sigma m\left\{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right\}.$$

That is $$\Sigma m\Sigma f\left(\frac{dx}{dt}\frac{dx'}{dt} + \frac{dy}{dt}\frac{dy'}{dt} + \frac{dz}{dt}\frac{dz'}{dt}\right)$$

$$+ \Sigma X\Sigma f(x'-x) + \Sigma Y\Sigma f(y'-y) + \Sigma Z\Sigma f(z'-z)$$

$$+ \Sigma m\Sigma r\frac{df}{dr}\left(\lambda\frac{dx}{dt} + \mu\frac{dy}{dt} + \nu\frac{dz}{dt}\right)\left(\lambda\frac{dx'}{dt} + \mu\frac{dy'}{dt} + \nu\frac{dz'}{dt}\right)$$

$$= 0 \;\ldots\ldots\ldots\; (\text{IV}).$$

55. Now if there are no intermolecular forces,

$$\Sigma X\Sigma f(x'-x) + \Sigma Y\Sigma f(y'-y) + \Sigma Z\Sigma f(z'-z)$$

is for an infinite system negligible, and equation IV. is satisfied, whatever f may be, by making

$$\frac{dx}{dt}\frac{dx'}{dt} + \frac{dy}{dt}\frac{dy'}{dt} + \frac{dz}{dt}\frac{dz'}{dt} = 0,$$

and $$\left(\lambda\frac{dx}{dt} + \mu\frac{dy}{dt} + \nu\frac{dz}{dt}\right)\left(\lambda\frac{dx'}{dt} + \mu\frac{dy'}{dt} + \nu\frac{dz'}{dt}\right) = 0,$$

on average for each value of r, and therefore for each value of f. This expresses condition A, which thus appears as a consequence of there being no intermolecular forces.

56. But if there are intermolecular forces, we shall find that condition A cannot exist.

In the limiting case when the encounters are binary, or no molecule is within the sphere of action of more than one other molecule at the same time, we have

$$X\Sigma f(x'-x) + Y\Sigma f(y'-y) + Z\Sigma f(z'-z) = -Rrf.$$

In the general case consider a spherical shell of radii $r \ldots r+dr$ described about m. Let R be the intermolecular force between m and a molecule m' within the shell, θ the angle made with x by the line mm' drawn from m to m'. Let f_r be the value of f for the radius r, and let Σ_r denote summation for all molecules m' within the shell. Then if X, &c. relate only to the forces exerted on m by molecules within the shell,

$$X\Sigma f(x'-x) = -f_r Rr\,(\Sigma_r \cos\theta)^2,$$

the mean value of which, if the molecules be distributed through the shell at haphazard, is $-\frac{1}{3}\Sigma_r Rr$.

Again X includes, not only the forces acting on m due to the molecules in the shell $r \ldots r+dr$, but also all other intermolecular forces acting on m, *e.g.* forces due to molecules within the shell $r' \ldots r'+dr'$, which forces we will denote by R'. The part of $X\Sigma f(x'-x)$ due to these forces is

$$-f_r R' r \Sigma_r \cos\theta \Sigma_{r'} \cos\theta',$$

where θ' corresponds to θ above. If we assume

$$\Sigma_r \cos\theta \Sigma_{r'} \cos\theta' = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1),$$

on average, we shall have

$$X\Sigma f(x'-x) = -\tfrac{1}{3}\Sigma_r Rrf.$$

But whether $X\Sigma f(x'-x)$ be equal to $-\frac{1}{3}\Sigma_r Rrf$ or not, it is nevertheless negative, and not zero. What has been proved for X is equally true for Y and for Z. So that

$$X\Sigma f(x'-x) + Y\Sigma f(y'-y) + Z\Sigma f(z'-z)$$

is in any case negative, and in the limiting case of binary encounters, or wherever we can assume (1), is equal to $-\Sigma Rrf$.

Since, as we have seen, in equation IV. the term

$$\Sigma X \Sigma f(x'-x) + \&c.$$

is negative and not zero, it follows that the sum of the remaining two terms, that is,

$$\Sigma m\Sigma f\left(\frac{dx}{dt}\frac{dx'}{dt}+\frac{dy}{dt}\frac{dy'}{dt}+\frac{dz}{dt}\frac{dz'}{dt}\right)$$
$$+\Sigma m\Sigma r\frac{df}{dr}\left(\lambda\frac{dx}{dt}+\mu\frac{dy}{dt}+\nu\frac{dz}{dt}\right)\left(\lambda\frac{dx'}{dt}+\mu\frac{dy'}{dt}+\nu\frac{dz'}{dt}\right),$$

is positive and not zero. But this is inconsistent with condition A. It follows that we must discard condition A when intermolecular forces exist.

57. First solution of equation IV. Let for any value of r

$$m\left(\frac{dx}{dt}\Sigma_r\frac{dx'}{dt}+\frac{dy}{dt}\Sigma_r\frac{dy'}{dt}+\frac{dz}{dt}\Sigma_r\frac{dz'}{dt}\right)=4\pi r^2\rho\phi \text{ on average,}$$

where ϕ is a function of r such that $4\pi r^3\phi$, and therefore also $4\pi r^3\phi f$, vanishes at either limit, when r is zero or infinite. Also assume all terms of the form $\frac{dx}{dt}\frac{dy'}{dt}$, &c. to be zero on average. Then as in Art. 54,

$$m\Sigma r\frac{df}{dr}\left(\lambda\frac{dx}{dt}+\mu\frac{dy}{dt}+\nu\frac{dz}{dt}\right)\left(\lambda\frac{dx'}{dt}+\mu\frac{dy'}{dt}+\nu\frac{dz'}{dt}\right)$$
$$=\tfrac{1}{3}\Sigma\phi r\frac{df}{dr}, \text{ because } \overline{\lambda^2}=\overline{\mu^2}=\overline{\nu^2}=\tfrac{1}{3}$$
$$=\tfrac{1}{3}\int_0^\infty 4\pi r^3\rho\phi\frac{df}{dr}\,dr$$
$$=-\int_0^\infty 4\pi r^2\rho\phi f dr-\tfrac{1}{3}\int_0^\infty 4\pi r^3\rho\frac{d\phi}{dr}f dr,$$

and using this in IV. we find

$$\Sigma X\Sigma f(x'-x)+\&c.-\tfrac{1}{3}\Sigma\int_0^\infty 4\pi r^3\rho\frac{d\phi}{dr}f dr=0,$$

which is satisfied by assuming for every r

$$\Sigma_r\{X(x'-x)+Y(y'-y)+Z(z'-z)\}=\tfrac{1}{3}4\pi r^3\rho\frac{d\phi}{dr};$$

also $$\int_0^\infty 4\pi r^2\rho\phi dr=-\tfrac{1}{3}\int_0^\infty 4\pi r^3\rho\frac{d\phi}{dr}\,dr,$$

whence $$\int_0^\infty 4\pi r^2\rho\phi dr=\Sigma Rr,$$

in all cases in which we can assume (1).

Second solution of equation IV. Since f is arbitrary we may equate separately to zero the term in IV. involving $r\frac{df}{dr}$, and the sum of the two terms involving f. That is, we make for each value of r,

$$\Sigma_r\left(\lambda\frac{dx}{dt}+\mu\frac{dy}{dt}+\nu\frac{dz}{dt}\right)\left(\lambda\frac{dx'}{dt}+\mu\frac{dy'}{dt}+\nu\frac{dz'}{dt}\right)=0\ldots\text{(IV a)},$$

and

$$m\left\{\frac{dx}{dt}\Sigma_r\frac{dx'}{dt}+\frac{dy}{dt}\Sigma_r\frac{dy'}{dt}+\frac{dz}{dt}\Sigma_r\frac{dz'}{dt}\right\}$$
$$+X\Sigma_r(x'-x)+Y\Sigma_r(y'-y)+Z\Sigma_r(z'-z)=0\ldots\text{(IV b)},$$

in which X includes the intermolecular forces acting on m due to molecules at whatever distance, but $x'-x$, &c. relate to a particular distance r.

The result (IV b) and the first solution show that the velocities of m' molecules distant r from m are *correlated* with that of m, or

$$m\left(\frac{dx}{dt}\Sigma_r\frac{dx'}{dt}+\frac{dy}{dt}\Sigma_r\frac{dy'}{dt}+\frac{dz}{dt}\Sigma_r\frac{dz'}{dt}\right)>0, \text{ on average.}$$

And the *correlation* is a function of r.

In this solution $4\pi r^2\rho\phi$, and in the former one $-\frac{1}{3}4\pi r^3\rho\,\frac{d\phi}{dr}$, is a determinate part of the Virial of the intermolecular forces acting on m, though not necessarily equal to Rr, except in cases where (1) can be assumed.

When r exceeds the "radius of action" of the molecule m, and so $R=0$, X nevertheless includes the x force due to molecules distant r' from m, for which R' is not zero. But ultimately as r increases, $\Sigma_r\cos\theta\,\Sigma_{r'}\cos\theta'=0$ for all values of r' for which R' is sensible. So that as r increases,

$$m\frac{dx}{dt}\Sigma_r\frac{dx'}{dt}+\text{\&c. becomes in any case zero.}$$

But the correlation may possibly retain a sensible value at distances from m greater than its radius of action.

Equation (IV a) expresses that although the velocity of m is correlated with that of m', yet it is not on average correlated with the velocity of m' resolved in direction mm', that is not correlated with $\lambda\frac{dx'}{dt}+\mu\frac{dy'}{dt}+\nu\frac{dz'}{dt}$. For (IV a) with (IV b) the simplest, though not perhaps the best, solution is the following.

If mP represent in magnitude and direction the velocity of m, and if it be taken for polar axis of a sphere of radius r described about m as centre, then the average motion of molecules on the surface of that sphere is on the meridian towards P, and proportional to the sine of the colatitude.

58. If the force R be attractive instead of being repulsive, $\frac{dx}{dt}\frac{dx'}{dt}$ + &c. will be negative instead of positive. The velocities of m and m' may be said in this case to be *contrarelated*. If there be two sets of molecules, A and B, and every A repels every other A, every B repels every other B, but A and B attract each other, the system will tend to form at every point two streams, the A's moving in one direction, and the B's in the opposite, which we may compare,

'si parva licet componere magnis,'

with the mutually attracting and repelling electricities supposed to constitute an electric current.

It should be noted that for any molecule m,

$$\tfrac{1}{2}m\Sigma\left(\frac{dx}{dt}\frac{dx'}{dt} + \&c.\right),$$

the summation including all values of r, is if (1) be assumed equal to the Virial, taken as positive when the forces are repulsive, of the intermolecular forces acting on m. (See Art. 85.)

I have treated $\overline{\frac{dx}{dt}\frac{dx'}{dt}}$ as zero in the absence of intermolecular forces. Strictly, n the number of molecules in the system being finite, and the centre of inertia at rest, it must be negative, but it may be neglected when n is great.

59. I have thus proved that if there be finite intermolecular forces, condition A cannot prevail, and

$$\frac{dx}{dt}\frac{dx'}{dt} + \frac{dy}{dt}\frac{dy'}{dt} + \frac{dz}{dt}\frac{dz'}{dt}$$

has on average a finite value, a function of r, and is positive if the forces are repulsive. The investigation does not apply to elastic spheres, in which the intermolecular forces are infinite during collision. I shall therefore devote the two following chapters to proving the same thing for equal elastic spheres by an independent method. It will be, I regret to say, a much more laborious method. If however the reader is now satisfied that I have established my case for finite intermolecular forces, he will have little difficulty in provisionally taking for granted that the same thing can by some means or other be established for the limiting case of elastic spheres, in which the forces become infinite for very small values of r. And omitting Chapter V. proceed at once to Chapter VI.

CHAPTER V.

CORRELATION OF VELOCITIES. ELASTIC SPHERES.

60. I PROPOSE in this chapter to prove for elastic spheres a proposition corresponding to that proved in the last chapter for molecules between which finite forces act. The elastic spheres shall be each of unit mass and diameter c. The same proposition for spheres of unequal masses or diameters is much more laborious, and when proved does not bring us much nearer to any probable form of molecule.

Equal Elastic Spheres.

Assume the chance that a group of n spheres shall simultaneously have component velocities

$$\left.\begin{array}{l}\alpha_1 \ldots \alpha_1 + d\alpha_1\\ \beta_1 \ldots \beta_1 + d\beta_1\\ \gamma_1 \ldots \gamma_1 + d\gamma_1\end{array}\right\}\text{ for the first}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\left.\begin{array}{l}\alpha_n \ldots \alpha_n + d\alpha_n\\ \beta_n \ldots \beta_n + d\beta_n\\ \gamma_n \ldots \gamma_n + d\gamma_n\end{array}\right\}\text{ for the } n\text{th}$$

to be

$$C\epsilon^{-hQ}d\alpha_1 \ldots d\gamma_n.$$

If we assume condition A, we virtually assume that

$$Q = \Sigma(\alpha^2 + \beta^2 + \gamma^2).$$

Now it will be found that when the diameters are finite the motion is not stationary when

$$Q = \Sigma\,(\alpha^2 + \beta^2 + \gamma^2),$$

but becomes stationary when

$$Q = \Sigma\,(\alpha^2 + \beta^2 + \gamma^2) + \Sigma\Sigma b\,(\alpha\alpha' + \beta\beta' + \gamma\gamma').$$

Here α, α', &c., are component velocities at the instant considered of any pair of spheres, and b is a function of the distance between them at that instant which, except for very small distances, is evanescent. I admit of course that given condition A always existing, the distribution of velocities among the spheres denoted by $\epsilon^{-h\Sigma(\alpha^2+\beta^2+\gamma^2)}$ is not disturbed by collisions. That has been proved many times. But the point is that condition A itself cannot continue to exist when collisions take place. In order that it may continue to exist, it is necessary that the system be continually receiving disturbances, or else that the diameters of the spheres shall be infinitely small, so that no collisions occur.

Definitions.

61. Let P be any point, r the distance of any other point from P. Let f be a function of r satisfying the following conditions, namely,

(1) f is equal to unity at all points within a small sphere of radius a described about P as centre.

(2) f is finite, positive and continuous everywhere.

(3) f is of negative degree at all points outside of the 'a' sphere and such that the series denoted by Σf, or $\int_a^\infty 4\pi r^2 f dr$, is ultimately convergent, but contains no high powers of $\frac{1}{r}$.

We may take for 'a' the radius of a sphere which on average contains one molecule.

Let now $\xi = \frac{\Sigma\alpha f}{\Sigma f}$, $\eta = \frac{\Sigma\beta f}{\Sigma f}$, $\zeta = \frac{\Sigma\gamma f}{\Sigma f}$, the summation including all the molecules of the system, and f having for each molecule the value proper to its distance from P. Then ξ, η, ζ are continuous functions of x, y, z, the coordinates of P.

Let $M_{xz} = \iiint dxdydz\, \alpha\gamma \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)$, in which $\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)$ is the value of that function at a given instant within the element of volume $dxdydz$, $\alpha\gamma$ is the value of the product $\alpha\gamma$ for the molecule (if any) which is within that element, or the sum of those products for all molecules within the element if there be more than one, and the integration includes all space. Then, for any element of volume, $\alpha\gamma$ changes from instant to instant by the passage of molecules into or out of the element.

There are two analogous functions, namely,

$$M_{xy} = \iiint dxdydz\, \alpha\beta \left(\frac{d\xi}{dy} + \frac{d\eta}{dx}\right),$$

$$M_{yz} = \iiint dxdydz\, \beta\gamma \left(\frac{d\eta}{dz} + \frac{d\zeta}{dy}\right),$$

and also three others of the form

$$M_{xx} = \iiint dxdydz\, \alpha^2 \frac{d\xi}{dx} \text{ \&c.}$$

It will be sufficient in this chapter to deal with M_{xz}, and we may for the present drop the suffix, and write M for M_{xz}.

Summary of the Argument.

62. It is necessary first to treat of the case in which the molecules, though possessing finite mass, are of infinitely small dimensions, so that collisions between them will not occur. That being the case, the system will be in stationary motion if the velocities are distributed according to Maxwell's law, Q being a sum of squares only. This we may admit whatever views we may hold as to the possibility of any other law. I shall assume Maxwell's distribution to exist. It follows from Q being a sum of squares only, that the fact of any molecule, or any group of molecules having any given velocities, affords, if the whole number of molecules be infinite, no presumption whatever with regard to the velocities of any other molecules.

We then find for this system the mean values of ξ^2, $\left(\frac{d\xi}{dz}\right)^2$, &c. In this system of material points $\frac{dM}{dt} = 0$, which gives rise to equations A and B below. It is then proved that if, with the same masses, the spheres have finite diameter c, so that collisions occur, $\frac{dM}{dt}$, which was zero, becomes, if ξ^2, &c. retain the same mean values as before, positive, and the motion not stationary. But the motion must become stationary. Therefore in the system of finite spheres ξ^2, &c. cannot retain the same mean values as before. It follows that in this system Q in ϵ^{-hQ} cannot be the sum of squares of the velocities only.

A System of Material Points.

63. The chance that the molecules shall at any instant have for their component velocities in x, $\alpha_1 \dots \alpha_1 + d\alpha_1$, &c., is $A\epsilon^{-hQ} d\alpha_1 \dots d\alpha_n$, where A is a constant and in the system now considered

$$Q = \alpha_1^2 + \alpha_2^2 + \&c.$$

But from Art. 61,

$$\alpha_n f_n = \xi \Sigma f - \alpha_1 f_1 - \dots - \alpha_{n-1} f_{n-1}.$$

It conduces to simplicity to assume $f_n = 1$, but, as will be seen, it in no way affects our conclusions. That being assumed,

$$\alpha_n = \xi \Sigma f - \alpha_1 f_1 - \alpha_2 f_2 - \&c.$$

Substituting this value for α_n in Q, we obtain

$$Q = \xi^2 (\Sigma f)^2 + (1 + f_1^2)\,\alpha_1^2 + (1 + f_2^2)\,\alpha_2^2 + \&c.$$

$$- 2f_1\alpha_1 \xi \Sigma f - 2f_2\alpha_2 \xi \Sigma f - \&c.$$

$$+ 2f_1 f_2 \alpha_1 \alpha_2 + 2f_1 f_3 \alpha_1 \alpha_3 + \&c.$$

If we now integrate ϵ^{-hQ} for $\alpha_1 \dots \alpha_{n-1}$ successively with limits $\pm \infty$, we get the result next stated.

Let D be the determinant of the coefficients in Q, each of the coefficients of products being divided by 2, that is

$$D = \begin{vmatrix} (\Sigma f)^2 & -f_1\Sigma f & -f_2\Sigma f \dots \\ -f_1\Sigma f & (1+f_1^2) & f_1f_2 \dots \\ -f_2\Sigma f & f_1f_2 & (1+f_2^2)\dots \\ \dots\dots & \dots\dots & \dots\dots \end{vmatrix}.$$

Let D_{pq} be the minor formed by omitting the pth row and qth column. Similarly let D_{pqrs} be the minor formed by omitting rows p and r, and columns q and s. Then by integrating for $\alpha_1 \dots \alpha_{n-1}$, Q is reduced to $\frac{D}{D_{11}}\xi^2$, whence $\overline{\xi^2} = \frac{D_{11}}{2hD}$. See Appendix ($g$). Also by integrating for $\alpha_2 \dots \alpha_{n-1}$ only, Q is reduced to

$$\tfrac{1}{2}\frac{D_{11}}{D_{1221}}\alpha_1^2 + \frac{D_{12}}{D_{1221}}\alpha_1\xi + \tfrac{1}{2}\frac{D_{22}}{D_{1221}}\xi^2.$$

Again we find (see Appendix (g))

$$\left.\begin{aligned} D_{11} &= 1 + f_1^2 + f_2^2 + \dots f^2_{n-1} = \Sigma_1^n f^2 \text{ since } f_n^2 = 1, \\ D_{1221} &= \Sigma f^2 - f_1^2, \\ D_{1123} &= f_1 f_2, \\ D_{22} &= D_{33} = \&\text{c.} = D = (\Sigma f)^2, \\ D_{12} &= -f_1\Sigma f. \end{aligned}\right\} \quad (19).$$

We have then for the chance that α_1 and ξ shall lie within assigned limits irrespective of the values of $\alpha_2 \dots \alpha_{n-1}$ the expression $A\epsilon^{-hQ'}d\alpha_1 d\xi$ in which

$$Q' = q\alpha_1^2 - 2p\alpha_1\xi + r\xi^2,$$

and $\frac{\Sigma f^2}{\Sigma f^2 - f_1^2} = q, \quad \frac{f_1\Sigma f}{\Sigma f^2 - f_1^2} = p, \quad$ and $\frac{(\Sigma f)^2}{\Sigma f^2 - f_1^2} = r.$

We see now that the assumption $f_n = 1$ has not affected the result, because writing $\frac{f^2}{f_n^2}$ for f^2 does not alter p, q, or r.

64. Let now ξ be the value of that function at P the origin, $\xi + \partial\xi$ its value at a neighbouring point P'. Then at P', $\epsilon^{-hQ'}$ becomes $\epsilon^{-hQ'} + \partial\xi\frac{d}{d\xi}\epsilon^{-hQ'}$. And if ξ be very small, this is equal to $\epsilon^{-hQ'}(1 + 2hp\alpha_1\partial\xi)$.

But if at P, ξ is not negligible, we must use instead of α, β, γ the following functions, namely,

$$u = \alpha - \xi,\ v = \beta - \eta,\ w = \gamma - \zeta, \text{ whence } \alpha = u + \xi \text{ \&c.},$$

and $$Q' = q(u+\xi)^2 - 2p\,\overline{u+\xi}\,\xi + r\xi^2,$$

or $$Q' = qu^2 + 2\,\overline{q-p}\,\xi u + (q - 2p + r)\,\xi^2,$$

and let $$\epsilon^{-hQ'} = \phi(u\,\xi).$$

Then if $\phi(u\,\xi)$ be the value of this function at P, $\phi_1(u\,\xi)$ its value at P',

$$\phi_1(u\,\xi) - \phi(u\,\xi) = \partial\xi \frac{d}{d\xi}\phi(u\,\xi).$$

Again, let $\phi(u)\,du$ be the chance that at P u shall lie between u and $u + du$, whatever ξ may be, that is

$$\phi(u) = \int_{-\infty}^{\infty} d\xi\phi(u\,\xi),$$

and the same chance at P' is

$$\phi_1(u) = \int_{-\infty}^{\infty} d\xi\phi(u\,\xi) + \partial\xi\int_{-\infty}^{\infty} d\xi \frac{d}{d\xi}\phi(u\,\xi).$$

Also $$\frac{d}{d\xi}\phi(u\,\xi) = \left(\frac{d}{d\xi}\right)\phi(u\,\xi) - \frac{d}{du}\phi(u\,\xi),$$

if $\left(\frac{d}{d\xi}\right)$ denotes differentiation with u constant. Therefore

$$\phi_1(u) - \phi(u) = \partial\xi\int_{-\infty}^{\infty} d\xi\left(\frac{d}{d\xi}\right)\phi(u\,\xi) - \partial\xi\int_{-\infty}^{\infty} d\xi\frac{d}{du}\phi(u\,\xi).$$

But $$\int_{-\infty}^{\infty} d\xi\left(\frac{d}{d\xi}\right)\phi(u\,\xi) = 0,$$

because $\phi(u\,\xi)$ vanishes at either limit. Therefore

$$\phi_1(u) - \phi(u) = -\partial\xi\int_{-\infty}^{\infty} d\xi\frac{d}{du}\phi(u\,\xi)$$

$$= \partial\xi\int_{-\infty}^{\infty} d\xi\phi(u\,\xi)\,2h\,(qu + \overline{q-p}\,\xi).$$

And this is proportional to

$$\epsilon^{-h'u^2} 2h' u\partial\xi,$$

if
$$h' = h \frac{(\Sigma f)^2}{(\Sigma f)^2 + \Sigma f^2 - 2f_1 \Sigma f},$$
whence $\phi_1(u) = \phi(u)(1 + 2h' u \partial\xi)$.

65. Now with the above definition of M we may write $\frac{dM}{dt} = 0$, that is

$$\iiint dx dy dz \left\{ \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right) \frac{d}{dt} \alpha\gamma + \alpha\gamma \frac{d}{dt} \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right) \right\} = 0 \ldots (\mathrm{A}),$$

the summation being for all the elements of volume, each with its own $\alpha\gamma$ and its own $\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right)$.

Now we shall find that on average $\frac{d}{dt} \alpha\gamma$ is of the opposite sign to $\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right)$, and $\frac{d}{dt} \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right)$ is of the same sign with $\alpha\gamma$. So that $\frac{dM}{dt}$ consists of two series neither of which is zero, but which are equal and opposite.

66. Let us consider the plane of xz, and ξ as varying in direction z, ζ as varying in direction x. Let us first deal with $\frac{d\xi}{dz}$ only. Consider the two infinite planes $z = 0$ and $z = dz$, and suppose for a moment $\frac{d\xi}{dz}$ constant between them. The number of molecules at or near the plane $z = dz$ for which u, or $\alpha - \xi$, lies between u and $u + du$ exceeds the corresponding number at or near the plane $z = 0$ by the quantity

$$A e^{-h'u^2} du \, 2h'u \frac{d\xi}{dz} dz.$$

That follows from Art. 64. To fix the ideas let u be positive. Let us separate from this class of molecules those whose z velocity is γ, and suppose γ negative. Let us then call the separated class the class $(u\gamma)$. Then the number of molecules of the class $(u\gamma)$ which pass through the plane $z = dz$ per unit of area and time exceeds the number of the same class which pass through the plane $z = 0$ per unit of area and time by the quantity $A\epsilon^{-h'u^2}\,\epsilon^{-h\gamma}\,du 2h'u\gamma\,\frac{d\xi}{dz}\,dz$. And the number of molecules of the class $(u\gamma)$ which enter S the space between the planes per unit of time exceeds the number of the same class which pass out of S per unit of time by

$$-SA\epsilon^{-h'u^2}\,\epsilon^{-h\gamma^2}\,du d\gamma\, 2h'u\gamma\,\frac{d\xi}{dz},$$

which is positive because $u\gamma$ is negative.

If $SNdud\gamma$ be the number of the class $(u\gamma)$ within S, we have

$$\frac{dN}{dt}\,du d\gamma = -A\epsilon^{-h'u^2}\,\epsilon^{-h\gamma^2}\,du d\gamma\, 2h'u\gamma\,\frac{d\xi}{dz} \;\ldots\ldots(20).$$

But if $\overline{u\gamma}$ be the mean value of $u\gamma$ for all the molecules within S, u and γ now taking all possible values,

$$\overline{u\gamma} = \iint_{-\infty}^{+\infty} Nu\gamma\, du d\gamma \Big/ \iint_{-\infty}^{+\infty} N du d\gamma,$$

and therefore

$$\frac{d}{dt}\,\overline{u\gamma} = \iint u\gamma\,\frac{dN}{dt}\,du d\gamma \Big/ \iint N du d\gamma,$$

because $\qquad \frac{d}{dt}\iint N du d\gamma = 0$ on average,

$$= -A\iint \epsilon^{-h'u^2}\,\epsilon^{-h\gamma^2}\,2h'u^2\gamma^2 du d\gamma\,\frac{d\xi}{dz} \text{ by (20)}$$

$$= -\frac{1}{2h}\,\frac{d\xi}{dz}.$$

I have assumed in this proposition that the space S within which $\frac{d\xi}{dz}$ is constant, is the continuous space between two infinite parallel planes. That will not occur in fact. But it is not essential to the argument that S should have that shape, or that it should consist of one closed surface. The proposition holds equally if S consists of all those elements of volume for which at a given instant $\frac{d\xi}{dz}$ has the same value. And it is true *on average* for each element of volume.

67. Again,
$$\frac{d}{dt}\overline{u\gamma} = \frac{d}{dt}\overline{(\alpha - \xi)\gamma}$$
$$= \frac{d}{dt}\overline{\alpha\gamma} - \frac{d}{dt}\overline{\xi\gamma}.$$

Now a molecule moving within S with positive γ moves from less to greater ξ, $\frac{d\xi}{dz}$ being positive; if with negative γ, it moves from greater to less ξ. For all molecules moving within S, $\frac{d}{dt}\overline{\gamma\xi}$ is positive and equal to $\gamma^2 \frac{d\xi}{dz}$. If S be divided into parallelopipeds of base $dxdy$ and altitude PP'

$$\iiint \gamma^2 \frac{d\xi}{dz}\, dxdydz = \iint \gamma^2 (\xi_P - \xi_{P'})\, dxdy,$$

ξ_P and $\xi_{P'}$ being the values of ξ at the upper and lower surfaces of the parallelopiped. By the motion of all these molecules $\gamma\xi$ is increased.

But at the upper end where ξ is greater, molecules with positive γ pass out of the space, at the lower end they pass in. For negative γ the converse is the case. By these entries and exits $\overline{\gamma\xi}$ is therefore diminished at the rate $\iint \gamma^2 (\xi_P - \xi_{P'})\, dxdy$, or by the same quantity by which it is increased by the motion of the molecules within S. On the whole therefore if ξ alone vary

$$\frac{d}{dt}\overline{\gamma\xi} = 0.$$

And
$$\frac{d}{dt}\overline{\alpha\gamma} = \frac{d}{dt}\overline{u\gamma} + \frac{d}{dt}\overline{\gamma\xi}$$
$$= \frac{d}{dt}\overline{u\gamma}.$$

We have then from Art. 66,

$$\frac{d}{dt}\overline{\alpha\gamma} = -\frac{1}{2h}\frac{d\xi}{dz}.$$

Similarly, if ζ only vary, $\frac{d}{dt}\overline{\alpha\gamma} = -\frac{1}{2h}\frac{d\zeta}{dx}$,

and therefore if ξ and ζ both vary,

$$\frac{d}{dt}(\overline{\alpha\gamma}) = -\frac{1}{2h}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right) \quad\ldots\ldots\ldots\ldots\ldots(21),$$

and (A) becomes

$$\iiint dxdydz\left\{\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)\frac{d}{dt}\alpha\gamma-\frac{1}{2h}\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)^2\right\}=0 \quad \text{...(B).}$$

It follows that $\alpha\gamma\dfrac{d}{dt}\left(\dfrac{d\xi}{dz}+\dfrac{d\zeta}{dx}\right)$ must be on average positive, and equal to $\dfrac{1}{2h}\left(\dfrac{d\xi}{dz}+\dfrac{d\zeta}{dx}\right)^2$.

68. We must however consider the value of $\dfrac{d}{dt}\left(\dfrac{d\xi}{dz}+\dfrac{d\zeta}{dx}\right)$ more carefully thus:

Let P, P' be two points on a sphere S whose coordinates referred to the centre C are respectively x, y, z, and $x, y, -z$, so that PP' is an edge of the parallelopiped, whose base is $dxdy$ at x, y. Let $\xi_P, \xi_{P'}$ be the values of ξ at P, P' respectively. Then if S be the volume of the sphere, and $\overline{\dfrac{d\xi}{dz}}$ the mean value of $\dfrac{d\xi}{dz}$ within the sphere,

$$S\overline{\frac{d\xi}{dz}}=\iint dxdydz\frac{d\xi}{dz}=\iint dxdy\,(\xi_P-\xi_{P'}),$$

the integration $dxdydz$ being throughout the space S. Let the radius of S be 'a' (Art. 61). Then we may take $\overline{\dfrac{d\xi}{dz}}$ as equal to $\dfrac{d\xi}{dz}$ at C.

Suppose a molecule at C whose velocities are α, β, γ. The change with the time of $S\overline{\dfrac{d\xi}{dz}}$ due to the motion of that molecule is $\left(\alpha\dfrac{d}{dx}+\beta\dfrac{d}{dy}+\gamma\dfrac{d}{dz}\right)\iint dxdy\,(\xi_P-\xi_{P'})$. The change due to the motion of all external molecules is zero on average.

Let now f be the value of f referred to P as centre. Then $\xi_P=\dfrac{\Sigma f\alpha}{\Sigma f}$. And let f' be the value of f referred to P' as centre, so that $\xi_{P'}=\dfrac{\Sigma f'\alpha}{\Sigma f}$. Then due to the motion of the molecule at C

$$\frac{d}{dt}(\xi_P-\xi_{P'})=-\frac{1}{\Sigma f}\alpha\left(\alpha\frac{d}{dx}+\beta\frac{d}{dy}+\gamma\frac{d}{dz}\right)\left(\frac{df}{dz}-\frac{df'}{dz}\right),$$

because on average $\frac{d}{dt}\Sigma f = 0$ &c. The minus sign is here required because f is referred to P, and therefore $\frac{df}{dz}$ has the opposite sign to that which it would have if referred to C. That is, $\frac{df}{dz} = -\frac{z}{r}\frac{df}{dr}$.

Now to form equation (B) we shall have to multiply by $\alpha\gamma$. And that will make the terms in α, β disappear, because $\alpha^2\alpha\gamma = \alpha\beta\alpha\gamma = 0$, on average and therefore on average

$$-\alpha\gamma\frac{d}{dt}(\xi_P - \xi_{P'}) = \alpha^2\gamma^2\frac{1}{\Sigma f}\left(\frac{df}{dz} - \frac{df'}{dz}\right).$$

And therefore

$$-S\alpha\gamma\frac{d}{dt}\overline{\frac{d\xi}{dz}} = \alpha^2\gamma^2\frac{1}{\Sigma f}\iint dx\,dy\left(\frac{df}{dz} - \frac{df'}{dz}\right),$$

the integration being over so much of the plane of xy as is within S, that is $-\alpha\gamma\frac{d}{dt}\frac{d\xi}{dz} = \alpha^2\gamma^2\frac{1}{\Sigma f}\frac{1}{a}\frac{df}{da}$, $\frac{df}{da}$ being the value of $\frac{df}{dr}$ when $r = a$.

By symmetry

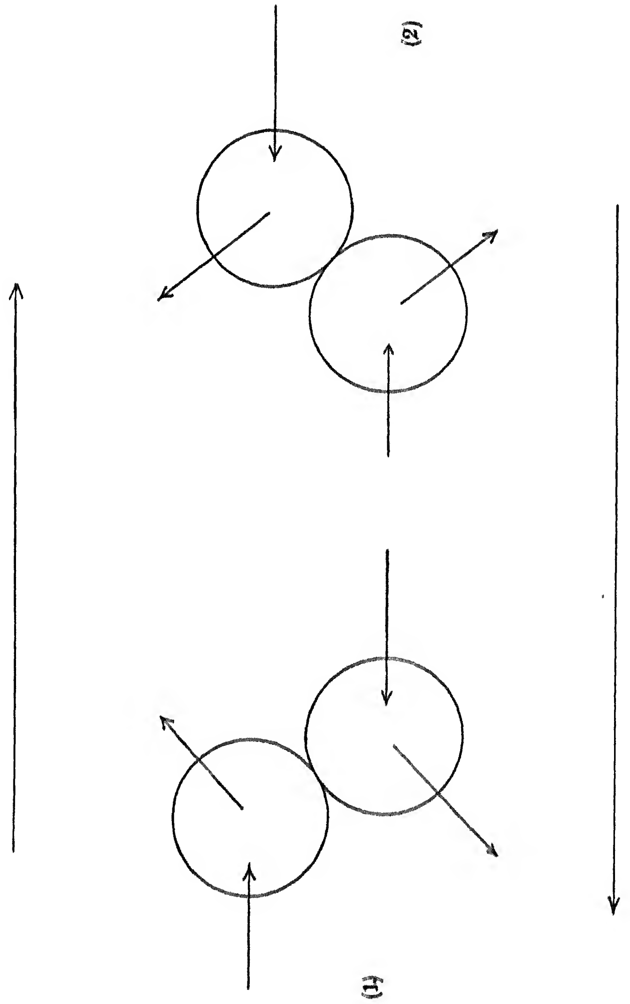
$$-\alpha\gamma\frac{d}{dt}\frac{d\zeta}{dx} = \alpha^2\gamma^2\frac{1}{\Sigma f}\frac{1}{a}\frac{df}{da}.$$

It follows from (A) and (B) that in stationary motion of the medium of material points on average

$$-2\alpha^2\gamma^2\frac{1}{\Sigma f}\frac{1}{a}\frac{df}{da} = \frac{1}{2h}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2 \text{..............(C)}.$$

Case of Spheres with Finite Diameters.

69. We now pass to the case in which our molecules, instead of being material points incapable of colliding with each other, become equal elastic spheres of finite diameter c. It will be shown that as the result of their collisions with each other, $\frac{dM}{dt}$, which in the system of material points was zero, becomes, so long at least as ξ^2, $\left(\frac{d\xi}{dz}\right)^2$, &c. retain the same values as before, positive, and the motion not stationary. It is worth while to show first in a general way by the aid of a diagram how this effect is produced by the collisions.



Let us take the plane of the paper for the plane of xz and suppose ξ alone to vary in z, $\frac{d\xi}{dz}$ being at a given instant positive near a certain point. That being the case, there is at the instant in question near that point a mean motion, or stream, of the molecules in direction x increasing as z increases. We may suppose this instantaneous stream to be positive for positive values of z, negative for negative values of z. It is indicated in the diagram by the long arrows.

Let us consider two kinds of collisions, (1) and (2), the directions of motion of either sphere before and after collision being shown by the small arrows. For simplicity these directions before collision are here drawn parallel to x.

If we examine collision (1), we see that the molecule which before collision was moving towards positive x is deflected upwards, *i.e.* towards the positive stream, and the molecule which before collision was moving towards negative x is deflected towards the negative stream. In either case the effect is to increase the stream *pro tanto.*

If we examine collision (2) we see that the reverse is the case. The effect of the collision is to diminish the stream. But now, $\frac{d\xi}{dz}$ being positive, there are more collisions of the kind (1) than of the kind (2) per unit of volume and time. And therefore collisions tend on the whole to increase the stream. For the same reason, it will be found, they make $\frac{dM}{dt}$ positive. It is true that in a rare medium the effect here indicated is very small. But the question is only of its sign, not of its magnitude.

70. Since every collision changes the direction of motion of the colliding spheres, the expression in Art. 66 derived from

$$\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)\frac{d(\alpha\gamma)}{dt}$$

contains, in addition to the result calculated in that article, a new term derived from collisions which we have now to calculate.

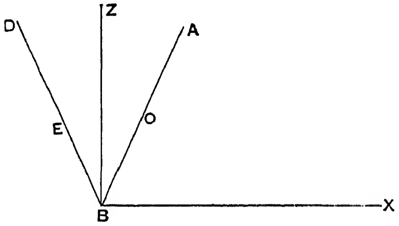
Let V be the half relative velocity of two molecules, λ, μ, ν its direction cosines before collision, λ', μ', ν' after collision. Let $\lambda V = V_x$, $\nu V = V_z$. The number of collisions per unit of volume and time for given V is $2\pi c^2 \rho V$. Hence, for the change with the time of $V_x V_z$ due to collisions with given V, we have

$$2\pi c^2 \rho V . V^2 (\overline{\lambda' \nu'} - \overline{\lambda \nu}),$$

the bar denoting mean values. We have now to find the values of $\overline{\lambda' \nu'}$ and $\overline{\lambda \nu}$ for all collisions, given V.

At the instant of collision let the centres of the two colliding molecules be A, B; so that AB is the line of centres. Let BD be the relative velocity. Or, if $DE = BE$, one molecule has velocity DE, and the other BE, in addition to the velocity of their common centre of inertia, whatever that may be. Let the angle $DBA = \theta$. If $AO = BO$, O is the point of contact.

Let BX, BZ be the directions of the axes of x and z, and let



the angle between the planes DBA and DBZ be ϕ, and the angle between the planes DBA and DBX be ϕ'.

Then, if x, y, z be the coordinates of A referred to O as origin, and if the direction DE be that of λ, μ, ν,

$$\left.\begin{aligned} z &= -\nu \frac{c}{2} \cos\theta + \frac{c}{2}\sqrt{1-\nu^2}\sin\theta\cos\phi, \\ x &= -\lambda \frac{c}{2} \cos\theta + \frac{c}{2}\sqrt{1-\lambda^2}\sin\theta\cos\phi' \end{aligned}\right\} \quad \ldots\ldots\ldots (22).$$

The complete definition of ϕ shall be this:—

When the plane *DBA*, turning round *DB*, contains the axis of z, $\phi = 0$ for that position of *BA* which makes the least angle with the axis of positive z. And ϕ' has a corresponding definition for the axis of x (see Art. 72, *post*).

71. If ξ_0, ζ_0 be the values of ξ and ζ at O, then at A

$$\left.\begin{aligned} \xi - \xi_0 &= \frac{c}{2}(-\nu\cos\theta + \sqrt{1-\nu^2}\sin\theta\cos\phi)\frac{d\xi}{dz} \\ \zeta - \zeta_0 &= \frac{c}{2}(-\lambda\cos\theta + \sqrt{1-\lambda^2}\sin\theta\cos\phi')\frac{d\zeta}{dx} \end{aligned}\right\} \quad (23).$$

Then by the same reasoning as employed in Art. 67 the number per unit of volume of pairs of molecules whose components of half relative velocity are

$$V_x \ldots V_x + dV_x, \quad V_y \ldots V_y + dV_y, \quad V_z \ldots V_z + dV_z$$

is at A

$$\frac{2h}{\pi}\sqrt{\frac{2h'}{\pi}}\,\epsilon^{-2h'V_x^2}\,\epsilon^{-2h(V_y^2+V_z^2)}\,dV_x\,dV_y\,dV_z\,\{1+4h'V_x\overline{\xi-\xi_0}\}.$$

Here owing to the variation of ξ in z, V_x is involved asymmetrically with respect to V_y and V_z. Let us suppose now V constant, but the angles θ and ϕ to vary. The general mean value of V_xV_z is of course zero. But the mean value of V_xV_z, given V, in the asymmetrical system is to be found by integrating the above expression according to θ and ϕ, and is not zero. Let us denote the mean value of V_xV_z, or $\lambda\nu V^2$, for all values of θ and ϕ, V being constant, by (V_xV_z), the mean value of the same function when V also varies being denoted by $\overline{V_xV_z}$. We have then, treating ξ alone as varying,

$$(V_xV_z) = \frac{V^2}{\pi}\int_0^{\frac{1}{2}\pi} 2\sin\theta\cos\theta\,d\theta\int_0^{\pi} d\phi\,(1 + 4h'V_x(\xi - \xi_0))$$

in which $\xi - \xi_0$ has the value given in (23), and the general means of functions of V_x and V_z, or λV and νV, are taken after integration according to θ and ϕ. That is, writing V_x/V for λ &c.

$$
\begin{aligned}
(V_x V_z) = V_x V_z \int_0^{\frac{1}{2}\pi} 2 \sin\theta \cos\theta \, d\theta \\
+ \frac{1}{\pi} V_x^2 V_z \frac{d\xi}{dz} \int_0^{\frac{1}{2}\pi} d\theta \int_0^{\pi} d\phi \, 2 \sin\theta \cos\theta \, 4h' \frac{c}{2} \Big(- \frac{V_z}{V} \cos\theta \\
+ \frac{\sqrt{V_x^2 + V_y^2}}{V} \sin\theta \cos\phi \Big) \\
= - \frac{4h'c}{3} \frac{V_x^2 V_z^2}{V} \frac{d\xi}{dz} \quad \ldots\ldots\ldots\ldots (24),
\end{aligned}
$$

because the general mean value of $V_x V_z$, or $\lambda\nu V^2$, is zero.

We have thus proved that, on the average of all *colliding pairs* of spheres, $(V_x V_z)$ is before collision of the opposite sign to $\frac{d\xi}{dz}$ or $\frac{d\zeta}{dx}$. This does not depend on the result of collision. It is therefore true if, instead of being elastic spheres, the molecules be centres of force, or whatever be their form.

72. We have next to calculate the mean value for all collisions of $\lambda'\nu'$, or the value of $\lambda\nu$ after collision. This will depend on the form of the molecule, and we shall now deal only with elastic spheres. It will be found that $\overline{\lambda'\nu'}$ is of the same sign with $\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)$.

We use the same notation as before. When the plane *DBA* turns round *DB* until it contains the axis of z, let A_z, A_z', which are on opposite sides of *DB*, be the two positions in which that plane is cut by the circle which A describes. Let A_z be nearer to the positive axis of z than A_z'. Then, for A_z, $\phi = 0$; for A_z', $\phi = \pi$. Similarly, when the plane turning round *DB* contains the axis of x, A_x, A_x' are the two positions of A in that plane, and, if A_x be nearer than A_x' to the positive axis of x, $\phi' = 0$ for A_x, $\phi' = \pi$ for A_x'.

Let ϵ be the angle between the plane of *DB* and z and the plane of *DB* and x, so that $\phi' = \phi - \epsilon$, $\phi = \phi' + \epsilon$. It will be seen that, if $\lambda\nu$ is negative, $\cos\epsilon$ is positive; if $\lambda\nu$ is positive,

$\cos\epsilon$ is negative. In either case

$$\cos\epsilon = \frac{-\lambda\nu}{\sqrt{1-\lambda^2}\sqrt{1-\nu^2}}, \quad \sin\epsilon = \frac{\mu}{\sqrt{1-\lambda^2}\sqrt{1-\nu^2}};$$

we have then, to find λ' and ν',

$$\left.\begin{aligned} \nu' &= -\nu\cos 2\theta + \sqrt{1-\nu^2}\sin 2\theta\cos\phi, \\ \lambda' &= -\lambda\cos 2\theta + \sqrt{1-\lambda^2}\sin 2\theta\cos\phi' \end{aligned}\right\} \text{......(25)}.$$

Whence, substituting V_x' for $\lambda' V$, and V_z' for $\nu' V$, we derive the two symmetrical systems

$$\left.\begin{aligned} V_z' &= -V_z\cos 2\theta + \sqrt{V_x^2 + V_y^2}\sin 2\theta\cos\phi \\ V_x' &= -V_x\cos 2\theta - \frac{V_x V_z}{\sqrt{V_x^2 + V_y^2}}\sin 2\theta\cos\phi \\ V_z' &= -V_z\cos 2\theta - \frac{V_x V_z}{\sqrt{V_y^2 + V_z^2}}\sin 2\theta\cos\phi' \\ V_x' &= -V_x\cos 2\theta + \sqrt{V_y^2 + V_z^2}\sin 2\theta\cos\phi' \end{aligned}\right\} \text{...(26)}.$$

The term involving $\sin\epsilon$ will disappear in the subsequent integration, and is omitted. The above systems hold for all values of V_x and V_z.

73. We now find that for given V, taking into consideration only the variation of ξ, or $\frac{d\xi}{dz}$,

$$(V_x' V_z') = \frac{1}{\pi}\int_0^{\frac{1}{2}\pi} d\theta \int_0^{\pi} d\phi\, 2\sin\theta\cos\theta\,(1 + 4h'V_x\overline{\xi - \xi_0})\,V_x' V_z'.$$

But with the above values of λ', ν', or $\frac{V_x'}{V}$, $\frac{V_z'}{V}$,

$$\int_0^{\frac{1}{2}\pi} d\theta \int_0^{\pi} d\phi\, 2\sin\theta\cos\theta\, V_x' V_z' = 0,$$

as is easily seen. Therefore

$$(V_x' V_z') = \frac{1}{\pi}\int_0^{\frac{1}{2}\pi} d\theta \int_0^{\pi} d\phi\, 2\sin\theta\cos\theta\, 4h'V_x\overline{\xi - \xi_0}\, V_x' V_z'$$

$$= \frac{1}{\pi} 4h'c \int_0^{\frac{1}{2}\pi} d\theta \int_0^{\pi} d\phi \sin\theta\cos\theta\, V_x$$

$$\times \left\{-\frac{V_z}{V}\cos\theta + \frac{\sqrt{V_x^2 + V_y^2}}{V}\sin\theta\cos\phi\right\} V_x' V_z' \frac{d\xi}{dz},$$

by (23). In this expression we have to substitute from (26) the values of V_x' and V_z', and integrate according to θ and ϕ.

To effect the integration according to ϕ, we reject odd powers of ϕ, and for $\cos^2\phi$ write $\frac{\pi}{2}$. We have then

$$(V_x'V_z') = \frac{1}{\pi}\frac{d\xi}{dz} 4h'c \int_0^{\frac{1}{2}\pi} d\theta \int_0^{\pi} d\phi \sin\theta\cos\theta V_x$$

$$\times \left\{-\frac{V_z}{V}\cos\theta + \frac{\sqrt{V_x^2+V_y^2}}{V}\sin\theta\cos\phi\right\} V_x' V_z'$$

$$= \frac{1}{\pi}\frac{d\xi}{dz} 4h'c \int_0^{\frac{1}{2}\pi} d\theta \int_0^{\pi} d\phi \sin\theta\cos\theta V_x FGH,$$

where

$$F = \left\{-\frac{V_z}{V}\cos\theta + \frac{\sqrt{V_x^2+V_y^2}}{V}\sin\theta\cos\phi\right\},$$

$$G = (-V_z\cos 2\theta + \sqrt{V_x^2+V_y^2}\sin 2\theta\cos\phi),$$

$$H = \left(-V_x\cos 2\theta - \frac{V_xV_z}{\sqrt{V_x^2+V_y^2}}\sin 2\theta\cos\phi\right),$$

or

$$(V_x'V_z') = -\frac{d\xi}{dz} 4h'c \frac{V_x^2V_z^2}{V} \cdot \int_0^{\frac{1}{2}\pi} \sin\theta\cos^2\theta\cos^2 2\theta\, d\theta$$

$$+ \frac{d\xi}{dz} 4h'c \frac{V_x^2V_z^2}{V}\, \tfrac{1}{2}\int_0^{\frac{1}{2}\pi} \sin\theta\cos^2\theta\sin^2 2\theta\, d\theta$$

$$- \frac{d\xi}{dz} 4h'c \frac{V_x^2(V_x^2+V_y^2)}{V}\, \tfrac{1}{2}\int_0^{\frac{1}{2}\pi} \sin^2\theta\cos\theta\sin 2\theta\cos 2\theta\, d\theta$$

$$+ \frac{d\xi}{dz} 4h'c \frac{V_x^2V_z^2}{V}\, \tfrac{1}{2}\int_0^{\frac{1}{2}\pi} \sin^2\theta\cos\theta\sin 2\theta\cos 2\theta\, d\theta$$

$$= -\frac{d\xi}{dz} 4h'c \frac{V_x^2V_z^2}{V} \int_0^{\frac{1}{2}\pi} \sin\theta\cos^2\theta\cos^2 2\theta\, d\theta$$

$$+ \frac{d\xi}{dz} 4h'c \frac{V_x^2V_z^2}{V}\, \tfrac{1}{2}\int_0^{\frac{1}{2}\pi} \sin\theta\cos^2\theta\sin^2 2\theta\, d\theta$$

$$- \frac{d\xi}{dz} 4h'c\, V_x^2 V\, \tfrac{1}{2}\int_0^{\frac{1}{2}\pi} \sin^2\theta\cos\theta\sin 2\theta\cos 2\theta\, d\theta$$

$$+ \frac{d\xi}{dz} 4h'c \frac{V_x^2V_z^2}{V}\, \tfrac{1}{2}\int_0^{\frac{1}{2}\pi} \sin^2\theta\cos\theta\sin 2\theta\cos 2\theta\, d\theta$$

$$+\frac{d\xi}{dz}4h'c\,\frac{V_x^2V_z^2}{V}\,\tfrac{1}{2}\int_0^{\frac{1}{2}\pi}\sin^2\theta\cos\theta\sin 2\theta\cos 2\theta\,d\theta$$

$$=\frac{d\xi}{dz}\,4h'c\,\frac{V_x^2V_z^2}{V}\,\frac{-11+12-4}{3\,.\,5\,.\,7}+\frac{d\xi}{dz}\,4h'c\,\frac{2}{3\,.\,5\,.\,7}\,V_x^2V,$$

but
$$\frac{\overline{V_x^2}}{V^2}=\frac{1}{3},\quad \frac{\overline{V_x^2V_z^2}}{V_4}=\frac{1}{3\,.\,5},$$

or
$$\overline{V_x^2V}=5\,.\,\frac{\overline{V_x^2V_z^2}}{V}.$$

Hence the expression becomes

$$\frac{d\xi}{dz}\,4h'c\,\frac{V_x^2V_z^2}{V}\,\frac{-11+12-4+10}{3\,.\,5\,.\,7}$$

$$=\frac{1}{3\,.\,5}\cdot\frac{d\xi}{dz}\,4h'c\,\frac{V_x^2V_z^2}{V}.$$

By symmetry if we treat $\frac{d\zeta}{dx}$ as varying instead of $\frac{d\xi}{dz}$, we obtain the expression

$$\frac{1}{3\,.\,5}\,\frac{d\zeta}{dx}\,4h'c\,\frac{V_x^2V_z^2}{V},$$

and therefore, given V,

$$(V_x'V_z')=\frac{1}{3\,.\,5}\,4h'c\,\frac{V_x^2V_z^2}{V}\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right).$$

And therefore comparing this with (24)

$$(V_x'V_z')-(V_xV_z)=4h'c\,\frac{V_x^2V_z^2}{V}\left(\frac{1}{3}+\frac{1}{3\,.\,5}\right)\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)\text{......(27).}$$

74. To find the rate of change with the time of V_xV_z given V, we multiply the last expression by $2\pi c^2\rho V$ (V being the half relative velocity), that is by the number of collisions which take place with given V per unit of volume and time. Let us denote the change due to collisions by $\frac{\partial}{\partial t}$.

The result is, given V,

$$\frac{\partial}{\partial t}(V_xV_z)=8h'\pi c^3\rho\left(\frac{1}{3}+\frac{1}{3\,.\,5}\right)V_x^2V_z^2\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right).$$

And then we introduce the factor

$$\sqrt{\frac{2h'}{\pi}\frac{2h}{\pi}}\,\epsilon^{-2h'V_x^2}\,\epsilon^{-2h(V_y^2+V_z^2)}\,dV_x dV_y dV_z,$$

and integrate for all values of V_x, V_y, V_z and so we obtain

$$\frac{\partial}{\partial t}\overline{V_x V_z} = \frac{1}{2h}\left(\frac{1}{3}+\frac{1}{3\,.\,5}\right)\pi c^3\rho\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right).$$

75. This being the value of $\frac{\partial}{\partial t}\overline{V_x V_z}$, what is the value of $\frac{d}{dt}(\alpha\gamma)$?

If U_x, U_y, U_z be the components of the common velocity of the two spheres, α, β, γ the velocities of one, α', β', γ' those of the other,

$$\alpha = U_x + V_x, \qquad \alpha' = U_x - V_x,$$
$$\beta = U_y + V_y, \qquad \beta' = U_y - V_y,$$
$$\gamma = U_z + V_z, \qquad \gamma' = U_z - V_z.$$

Therefore $\quad \alpha\gamma + \alpha'\gamma' = 2\,(U_x U_z + V_x V_z).$

Hence since U_x, U_y, U_z do not vary by collision,

$$\frac{\partial}{\partial t}(\alpha\gamma + \alpha'\gamma') = 2\frac{\partial}{\partial t}\overline{V_x V_z} \quad \text{..............(28).}$$

It follows that on average of all collisions

$$\frac{\partial}{\partial t}(\alpha\gamma) = \frac{\partial}{\partial t}\overline{V_x V_z}$$
$$= \frac{1}{2h}\pi c^3\rho\left(\frac{1}{3}+\frac{1}{3\,.\,5}\right)\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right),$$

and therefore on average

$$\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)\frac{\partial}{\partial t}(\alpha\gamma) = \frac{1}{2h}\pi c^3\rho\left(\frac{1}{3}+\frac{1}{3\,.\,5}\right)\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)^2 \text{......(C}_1\text{).}$$

76. We have next to consider the change in the term $\alpha\gamma\frac{d}{dt}\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)$ due to the variation of α, or γ by collisions. As before let us treat ξ only as varying. Let us use the construction of Art. 68. Consider two spheres in collision their point of contact being at C the centre of the a sphere. The z ordinates of their centres are

$$\frac{c}{2}(-\nu\cos\theta+\sqrt{1-\nu^2}\sin\theta\cos\phi),$$

and
$$\frac{c}{2}(-\nu\cos\theta+\sqrt{1-\nu^2}\sin\theta\cos\phi).$$

To find the value of $\frac{\partial}{\partial t}\xi_P$ due to the collision, let us refer f to the point P. Its value at the point of contact being f, its value at the centres of the two spheres respectively is

$$f+\frac{c}{2}(-\nu\cos\theta+\sqrt{1-\nu^2}\sin\theta\cos\phi)\frac{df}{dz},$$

and
$$f-\frac{c}{2}(-\nu\cos\theta+\sqrt{1-\nu^2}\sin\theta\cos\phi)\frac{df}{dz},$$

with corresponding terms in $\frac{df}{dx}$ and $\frac{df}{dy}$ which will disappear on integration.

Now for the first sphere α is increased by the collision by $V_x'-V_x$, for the second it is diminished by the same quantity. Therefore as the result of this collision

$$\partial\xi_P=\partial\frac{\Sigma\alpha f}{\Sigma f}=-\frac{1}{\Sigma f}c\frac{df}{dz}(-\nu\cos\theta+\sqrt{1-\nu^2}\sin\theta\cos\phi)(V_x'-V_x).$$

For the minus sign here introduced see Art. 68.

Substitute for $V_x'-V_x$ its value from (26), multiply by $2\sin\theta\cos\theta$, and integrate according to θ and ϕ. That gives

$$\Sigma f\partial\xi_P=-\frac{1}{\pi}c\frac{df}{dz}V\int_0^{\frac{1}{2}\pi}d\theta\int_0^{\pi}d\phi\,2\sin\theta\cos\theta FG,$$

where
$$F=\{-\nu\cos\theta+\sqrt{1-\nu^2}\sin\theta\cos\phi\},$$

$$G=\left(-\lambda\,2\cos^2\theta-\frac{\lambda\nu}{\sqrt{1-\nu^2}}\sin 2\theta\cos\phi\right).$$

That is
$$\Sigma f\partial\xi_P=-\frac{8}{15}c\frac{df}{dz}\lambda\nu V.$$

Now multiply by $2\pi c^2\rho V$, the number of collisions given V per unit of volume and time. That gives

$$\frac{\partial\xi_P}{\partial t}=-\frac{16}{15}\pi c^3\rho\,\overline{V_xV_z}\,\frac{1}{\Sigma f}\frac{df}{dz}.$$

Similarly $$\frac{\partial \xi_{P'}}{\partial t} = -\frac{16}{15}\pi c^3 \rho V_x V_z \frac{1}{\Sigma f}\frac{df'}{dz},$$

and $$\frac{\partial}{\partial t}(\xi_P - \xi_{P'}) = -\frac{16}{15}\pi c^3 \rho V_x V_z \frac{1}{\Sigma f}\left(\frac{df}{dz} - \frac{df'}{dz}\right),$$

and $$\frac{\partial}{\partial t}\iint dx dy\,(\xi_P - \xi_{P'}) = -\frac{16}{15}\pi c^3 \rho V_x V_z \iint dx dy \frac{1}{\Sigma f}\left(\frac{df}{dz} - \frac{df'}{dz}\right)$$
$$= -\frac{16}{15}\pi c^3 \rho V_x V_z \frac{1}{\Sigma f}\frac{1}{a}\frac{df}{da} S,$$

where the integrations are throughout the section of the 'a' sphere made by the plane of xy, S is the volume of the a sphere, and $\frac{1}{a}\frac{df}{da}$ is the value of $\frac{1}{r}\frac{df}{dr}$ when $r = a$.

But $$\frac{1}{S}\iint dx dy\,(\xi_P - \xi_{P'}) = \frac{d\xi}{dz},$$

as in Art. 68, therefore

$$\frac{\partial}{\partial t}\frac{d\xi}{dz} = -\frac{16}{15}\pi c^3 \rho V_x V_z \frac{1}{\Sigma f}\frac{1}{a}\frac{df}{da}.$$

Similarly $$\frac{\partial}{\partial t}\frac{d\zeta}{dx} = -\frac{16}{15}\pi c^3 \rho V_x V_z \frac{1}{\Sigma f}\frac{1}{a}\frac{df}{da},$$

and $$\frac{\partial}{\partial t}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right) = -\frac{32}{15}\pi c^3 \rho V_x V_z \frac{1}{\Sigma f}\frac{1}{a}\frac{df}{da}.$$

This expresses the change of $\frac{d\xi}{dz} + \frac{d\zeta}{dx}$ due to collision between two spheres. Let α, β, γ be the velocities of one of the two colliding spheres, α', β', γ' those of the other.

Then $\frac{dM}{dt}$ contains the two terms

$$\alpha\gamma\frac{\partial}{\partial t}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right) + \alpha'\gamma'\frac{\partial}{\partial t}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right).$$

But $$\alpha = U_x + V_x \qquad \alpha' = U_x - V_x$$
$$\gamma = U_z + V_z \qquad \gamma' = U_z - V_z,$$

as in Art. 75.

Therefore $(\alpha\gamma + \alpha'\gamma')\, V_x V_z = 2 V_x^2 V_z^2$ on average,

because $U_x U_z V_x V_z = 0$ on average.

Therefore for each sphere separately

$$\alpha\gamma \frac{\partial}{\partial t}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right) = -\frac{32}{15}\pi c^3 \rho V_x^2 V_z^2 \frac{1}{a}\frac{df}{da} \text{ on average}$$

$$= -\frac{8}{15}\pi c^3 \rho \alpha^2 \gamma^2 \frac{1}{a}\frac{df}{da},$$

because
$$\alpha^2\gamma^2 = U_x^2 U_z^2 + V_x^2 V_z^2 + U_x^2 V_z^2 + U_z^2 V_x^2$$
$$= 4 V_x^2 V_z^2 \text{ on average.}$$

We have then on average, remembering Art. 68 ...... (C),

$$\alpha\gamma \frac{\partial}{\partial t}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right) = \frac{4}{15}\pi c^3 \rho \frac{1}{2h}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2 \text{ .... } (C_2).$$

Adding this to C_1, we find for the term in $\frac{dM}{dt}$ due to collisions,

$$\frac{\partial M}{\partial t} = \frac{2}{3}\pi c^3 \rho \iiint dx\,dy\,dz\, \frac{1}{2h}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2 \text{ ......} (C_3).$$

We interpret this as follows. As the result of collisions, molecules moving in a given direction, as that of x, are on average deflected towards that side where the average motion of the molecules, that is the stream, is for the time being in x. And so collisions tend to increase the stream. Compare Art. (57).

77. Now referring to equation (A), we see that $\frac{dM}{dt}$, which in the medium of material points was zero, and so the motion stationary, has, when the spheres have finite diameter, become positive, namely

$$\frac{dM}{dt} = \iiint dx\,dy\,dz \left\{ \alpha\gamma \frac{d}{dt}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right) - \frac{1}{2h}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2 + \frac{2}{3}\pi c^3 \rho \frac{1}{2h}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2 \right\} \text{ ....} (D),$$

of which the first two terms are together zero, as in (A), and the third is positive. Therefore if in the system of spheres of finite diameter $\left(\frac{\overline{d\xi}}{dz}\right)^2$ &c. have the same values as in the system of material points, $\frac{dM}{dt}$ is positive.

But in stationary motion $\frac{dM}{dt}$ must be zero. Therefore in stationary motion of the system of finite spheres $\left(\frac{\overline{d\xi}}{dz}\right)^2$ &c., cannot have the same mean values which they have in the system of material points.

78. It might be suggested that the explanation of the difficulty consists in the fact that when the molecules have finite diameters the quantity of momentum transferred across any plane per unit of area and time is increased in a certain ratio, $1 : 1 + \frac{1}{2}\kappa$, where, in the case of elastic spheres, $\kappa = \frac{2}{3}\pi c^3\rho$. But this increases both terms in (A) in the same ratio, and therefore, so far as this property is concerned, $\frac{dM}{dt}$ remains zero. This effect arises from the usual convention concerning elastic bodies, according to which there is on every collision an instantaneous transfer of momentum through a certain space. It has nothing to do with the change of direction of the relative velocity, which also occurs on collision, and which we now have considered. The first effect would take place in precisely the same way, if after every collision the direction of the relative velocity were restored by Maxwell's corps of demons to what it was before collision.

CHAPTER VI.

CORRELATION OF VELOCITIES. ELASTIC SPHERES.

79. THE solution of the problem of the last chapter is this. In the system of spheres of finite diameter ξ has become $\xi+\xi'$, and $\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)^2$ has become $\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)^2+\left(\frac{d\xi'}{dz}+\frac{d\zeta'}{dx}\right)^2$. That gives by arranging the terms in (D)

$$\frac{dM}{dt}=\iiint dxdydz\left\{\alpha\gamma\frac{d}{dt}\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)-\frac{1}{2h}\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)^2\right.$$

$$\left.+\frac{2}{3}\pi c^3\rho\frac{1}{2h}\left[\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)^2+\left(\frac{d\xi'}{dz}+\frac{d\zeta'}{dx}\right)^2\right]-\frac{1}{2h}\left(\frac{d\xi'}{dz}+\frac{d\zeta'}{dx}\right)^2\right\}.$$

We may assume that $\alpha\gamma\frac{d}{dt}\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)$ is not altered by the substitution of $\xi+\xi'$ for ξ, or $\alpha\gamma\frac{d}{dt}\left(\frac{d\xi'}{dz}+\frac{d\zeta'}{dx}\right)=0$.

The first two terms of this equation are together zero by (A) Art. 65. The remaining two terms can be made zero by suitably choosing the ratio of the means

$$\left(\overline{\frac{d\xi'}{dz}}+\overline{\frac{d\zeta'}{dx}}\right)^2:\left(\overline{\frac{d\xi}{dz}}+\overline{\frac{d\zeta}{dx}}\right)^2.$$

We have, namely, writing κ for $\frac{2}{3}\pi c^3\rho$,

$$\kappa\left\{\left(\overline{\frac{d\xi}{dz}}+\overline{\frac{d\zeta}{dx}}\right)^2+\left(\overline{\frac{d\xi'}{dz}}+\overline{\frac{d\zeta'}{dx}}\right)^2\right\}=\left(\overline{\frac{d\xi'}{dz}}+\overline{\frac{d\zeta'}{dx}}\right)^2,$$

whence

$$\left(\overline{\frac{d\xi'}{dz}}+\overline{\frac{d\zeta'}{dx}}\right)^2=\frac{\kappa}{1-\kappa}\left(\overline{\frac{d\xi}{dz}}+\overline{\frac{d\zeta}{dx}}\right)^2=\kappa\left(\overline{\frac{d\xi}{dz}}+\overline{\frac{d\zeta}{dx}}\right)^2\quad\ldots(29),$$

if κ^2, κ^3 &c. are negligible.

80. Instead of using $M_{xz} = \iiint dxdydz\alpha\gamma\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)$, or the analogous terms M_{xy} or M_{yz}, we may make use of

$$M_{xx} = \iiint dxdydz\alpha^2\frac{d\xi}{dx},$$

or the analogous terms M_{yy} or M_{zz}, and we obtain the same result. I have set out the mathematical work in the Appendix by reference to Arts. 66, 68. We may therefore now use the complete expression for M, namely

$$\begin{aligned}M = \iiint dxdydz\Big\{&\alpha^2\frac{d\xi}{dx} + \beta^2\frac{d\eta}{dy} + \gamma^2\frac{d\zeta}{dz}\\ &+ \alpha\beta\left(\frac{d\xi}{dy} + \frac{d\eta}{dx}\right) + \alpha\gamma\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)\\ &+ \beta\gamma\left(\frac{d\eta}{dz} + \frac{d\zeta}{dy}\right)\Big\} \quad\text{..............................(30)},\end{aligned}$$

and we then reduce $\frac{\partial M}{\partial t}$ to zero by making

$$\overline{\left(\frac{d\xi'}{dx}\right)^2} = \frac{\kappa}{1-\kappa}\overline{\left(\frac{d\xi}{dx}\right)^2},\quad \overline{\left(\frac{d\xi'}{dy}\right)^2} = \frac{\kappa}{1-\kappa}\overline{\left(\frac{d\xi}{dy}\right)^2}\ \text{\&c.}$$

Now so long as the distribution of velocities is represented by ϵ^{-hQ}, and Q is the sum of squares of the velocities, $\overline{\xi^2}$ &c. and $\overline{\left(\frac{d\xi}{dz}\right)^2}$ &c. must have either the same or less values than those found by the method of Art. 63, for material points. In stationary motion therefore in the system of finite spheres Q cannot be the sum of squares only. It must contain products of the form $b(\alpha\alpha' + \beta\beta' + \gamma\gamma')$. And the question now is, what must be the form of the coefficients b, or as I shall call them *coefficients of correlation*, in order that the ratio $\overline{\left(\frac{d\xi'}{dz}\right)^2} : \overline{\left(\frac{d\xi}{dz}\right)^2}$ may have the required value.

81. By way of illustration let us suppose n molecules within a sphere of radius R, their velocities being distributed according to Maxwell's law ϵ^{-hQ}, where Q is the sum of squares of the velocities, and let us impart to each molecule, in addition to the velocity which it has in that motion, the small velocity X' in x.

This being done, the chance that one of these molecules shall have velocity represented by lines drawn from the origin to some point or other within an element of volume $d\Omega$, whose centre is distant p from the origin in direction making the angle ψ with the axis of x, is

$$A\epsilon^{-hp^2}(1+2hpX'\cos\psi)\,d\Omega.$$

The chance that another molecule shall have velocity represented by lines drawn from the origin to some point or other with an element of volume $d\Omega'$ distant q from the origin, in direction making the angle ϕ with p, is

$$A\epsilon^{-hq^2}\,d\Omega'\,\{1+2hqX'(\cos\psi\cos\phi+\sin\psi\sin\phi\cos\epsilon)\},$$

where ϵ is the angle between the plane of p and q and the plane of p and x. The chance that both molecules shall have the velocities aforesaid is

$$A^2\epsilon^{-h(p^2+q^2)}\,d\Omega d\Omega'(1+2hpX'\cos\psi)\,\{1+2hqX'(\cos\psi\cos\phi \\ +\sin\psi\sin\phi\sin\epsilon)\}.$$

Multiply this by $\frac{1}{2}\sin\psi\,d\psi$, and integrate for all values of ϵ and ψ, and we obtain

$$A^2\epsilon^{-h(p^2+q^2)}\,d\Omega\,d\Omega'\left(1+\frac{4h^2}{3}X'^2pq\cos\phi\right),$$

expressing now the chance that the velocities p and q, of two molecules, in whatever direction either is, shall make the angle ϕ with each other. Now let u, v, w be the components of p; u', v', w' those of q. Then

$$p^2+q^2=u^2+v^2+w^2+u'^2+v'^2+w'^2,$$

$$d\Omega d\Omega'=du\,dv\,dw\,du'\,dv'\,dw',$$

$$pq\cos\phi=uu'+vv'+ww'.$$

Therefore, since, with these substitutions, the expression does not contain ϕ, it gives the chance that two molecules, both within the R sphere, shall respectively have velocities $u\ldots u+du$, &c., in the form

$$A^2\epsilon^{-h(u^2+v^2+w^2+u'^2+v'^2+w'^2)}\,du\ldots dw'\left\{1+\frac{4h}{3}X'^2(uu'+vv'+ww')\right\},$$

that is, assuming X'^2, &c., to be small,

$$A^2\epsilon^{-hQ'}\,du\ldots dw',$$

in which

$$Q' = u^2+v^2+w^2+u'^2+v'^2+w'^2-\frac{4h}{3}X'^2(uu'+vv'+ww').$$

Evidently, if we take Y' and Z' into account, we shall have to substitute $X'^2+Y'^2+Z'^2$ for X'^2 in the last expression.

We see then that in the case now treated the coefficient of correlation b has the form

$$b \doteq -\frac{4h}{3}(X'^2+Y'^2+Z'^2),$$

or, since $$\overline{X^2}+\overline{Y^2}+\overline{Z^2}=\frac{3}{2nh},$$

X, Y, Z denoting the velocities of the centre of inertia of the n molecules,

$$b=-\frac{2}{n}(X'^2+Y'^2+Z'^2)/(\overline{X^2}+\overline{Y^2}+\overline{Z^2}) \quad\ldots\ldots(31).$$

82. Next let us employ the converse method, namely, the coefficients b being supposed given, to find the ratio $\overline{\xi'^2}:\overline{\xi^2}$. And first let us consider a finite number of molecules, and all the b coefficients equal, and very small, so that b^2, b^3, &c., may be neglected.

We have generally, referring to the determinant of Art. 63, $\overline{\xi^2}=\frac{D_{11}}{2hD}$, and therefore

$$\overline{\xi^2}+\overline{\xi'^2}=\overline{\xi^2}+\partial\overline{\xi^2}$$
$$=\overline{\xi^2}+\partial\frac{D_{11}}{2hD},$$

$\partial\overline{\xi^2}$ being the variation of $\overline{\xi^2}$ due to the introduction of the b coefficients. Now it is proved in the Appendix (n) that in this case $\partial D=0$. Therefore

$$\overline{\xi'^2}=\partial\frac{D_{11}}{2hD}=\frac{\partial D_{11}}{2hD}.$$

Also
$$D_{11} = \begin{vmatrix} 1+f_1^2, & f_1f_2, & f_1f_3, \dots \\ f_1f_2, & 1+f_2^2, & f_2f_3, \dots \\ f_1f_3, & f_2f_3, & 1+f_3^2, \dots \\ \dots\dots & \dots\dots & \dots\dots \end{vmatrix}$$

and (see Art. 83) $\partial(1+f_1^2) = -bf_1$, $\partial(1+f_2^2) = -bf_2$, &c.,

$$\partial f_1f_2 = \tfrac{1}{2}(b - bf_1 - bf_2), \text{ \&c.}$$

If we were now to make every $f = 1$, we find that every constituent in D_{11} as it originally stood is in the varied form of D_{11} multiplied by $\frac{2-b}{2}$. Hence

$$\partial D_{11} = -D_{11}\left(1 - \left(\frac{2-b}{2}\right)^{n-1}\right) = -D_{11}\frac{n-1}{2}b.$$

But on the same assumption that every $f = 1$,

$$\frac{D_{11}}{2hD} = \frac{1}{2nh}.$$

And
$$\overline{\xi'^2} = \partial D_{11}/2hD = -\frac{1}{2nh}\frac{n-1}{2}b,$$

whence
$$\overline{\xi'^2} + \overline{\eta'^2} + \overline{\zeta'^2} = -\frac{3}{4h}\frac{n-1}{n}b$$
$$= -\frac{3}{4h}b,$$

n being large, or

$$b = -\frac{4h}{3}(\overline{\xi'^2} + \overline{\eta'^2} + \overline{\zeta'^2}),$$

as we obtained in a different way in Art. 81.

83. Next, let us assume b, the coefficient of correlation between the velocities of two molecules, to be a function of the distance r between the molecules to which it relates. And let it be required to find, on this hypothesis, the ratio

$$\overline{\xi'^2} : \overline{\xi^2}, \text{ or } \overline{\left(\frac{d\xi'}{dz}\right)^2} : \overline{\left(\frac{d\xi}{dz}\right)^2}.$$

For the system of finite spheres we shall have

$$Q = \Sigma\alpha^2 + \Sigma\Sigma b_{pq}\alpha_p\alpha_q,$$

where b_{pq} is the value of b for the two molecules whose velocities are α_p, α_q, &c., whence, substituting for α_n as in Art. 63,

$$\begin{aligned} Q = (1 + f_1^2 - b_{1n} f_1)\, \alpha_1^2 + (1 + f_2^2 - b_{2n} f_2)\, \alpha_2^2 + \&\text{c.} \\ - 2\alpha_1 \xi (1 - \tfrac{1}{2} b_{1n} \Sigma f) - \&\text{c.} \\ + 2 (f_1 f_2 + \tfrac{1}{2} b_{12} - \tfrac{1}{2} b_{1n} f_2 - \tfrac{1}{2} b_{2n} f_1)\, \alpha_1 \alpha_2 + \&\text{c.} \quad \ldots(32). \end{aligned}$$

Then
$$\overline{\xi^2} + \overline{\xi'^2} = \frac{D_{11} + \partial D_{11}}{2hD} = \xi^2 + \Sigma b \frac{dD_{11}}{db} \Big/ 2hD,$$

or
$$\overline{\xi'^2} = \Sigma b \frac{dD_{11}}{db} \Big/ 2hD,$$

every b being small, so that its square and higher powers may be neglected, and, for the same reason, the variation of D may be neglected, as will be easily found. Appendix (n).

Now in this case [see Appendix (o)]

$$\Sigma b \frac{dD_{11}}{db} = -\tfrac{1}{2} \Sigma\Sigma b_{pq} f_p f_q,$$

in which p and q respectively take all values from 1 to n, there being n molecules in the system. Also if we assume the molecules to be scattered through space without regard to the position of p, with density ρ, $\Sigma\Sigma b_{pq} f_p f_q$ may be represented by the integral

$$\Sigma f_p \int_c^\infty 4\pi r^2 \rho\, dr\, b_{pq} f_q;$$

and if b_{pq} is very small except for very small values of r_{pq} (see Appendix (p)), we find

$$\Sigma f_p \int_c^\infty 4\pi r^2 \rho\, b_{pq} f_q\, dr = \Sigma f_p^2 \int_c^\infty 4\pi r^2 \rho\, b_{pq}\, dr \quad \ldots\ldots(33),$$

$$= \Sigma f_p^2 \Sigma b, \text{ if } \Sigma b = \int_c^\infty 4\pi r^2 \rho\, b\, dr,$$

and therefore
$$\begin{aligned} \overline{\xi'^2} &= \partial \overline{\xi^2} \\ &= -\tfrac{1}{2} \Sigma f_p^2 \Sigma b / 2hD = -\tfrac{1}{2} \Sigma b \,.\, \overline{\xi^2}, \end{aligned}$$

because $\Sigma f_p^2 = D_{11}$; and if b be so chosen that $\tfrac{1}{2} \Sigma b = -\kappa$,

$$\overline{\xi'^2} = \kappa \overline{\xi^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(34).$$

84. Again, it can be shown that under the same conditions

$$\left(\frac{\overline{d\xi'^2}}{dz}\right) = \kappa\, \overline{\left(\frac{d\xi}{dz}\right)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(35),$$

and this is the required ratio.

For since
$$\xi = \alpha_1 \frac{f_1}{\Sigma f} + \alpha_2 \frac{f_2}{\Sigma f} + \&c.,$$
$$\frac{d\xi}{dz} = \alpha_1 \frac{d}{dz}\frac{f_1}{\Sigma f} + \alpha_2 \frac{d}{dz}\frac{f_2}{\Sigma f} + \&c.$$
$$= \alpha_1\theta_1 + \alpha_2\theta_2 + \ldots + \alpha_n\theta_n,$$

if
$$\theta_1 = \frac{d}{dz}\frac{f_1}{\Sigma f} \&c.,$$

whence
$$\alpha_n = \frac{1}{\theta_n} \cdot \frac{d\xi}{dz} - \alpha_1 \frac{\theta_1}{\theta_n} - \alpha_2 \frac{\theta_2}{\theta_n} - \&c.,$$

and
$$Q = \alpha_1^2 + \alpha_2^2 + \ldots + \alpha_n^2$$
$$= \frac{1}{\theta_n^2}\left(\frac{d\xi}{dz}\right)^2 + \left(1 + \frac{\theta_1^2}{\theta_n^2}\right)\alpha_1^2 + \&c. + \left(1 + \frac{\theta^2_{n-1}}{\theta_n^2}\right)\alpha^2_{n-1}$$
$$- \frac{2\theta_1}{\theta_n^2}\alpha_1 \frac{d\xi}{dz} - \&c.$$
$$+ \frac{2\theta_1\theta_2}{\theta_n^2}\alpha_1\alpha_2 + \&c.$$

Now the determinant of this expression differs from that of Art. 63 only in the form of the coefficients. Therefore
$$\overline{\left(\frac{d\xi}{dz}\right)^2} = \frac{D_{11}}{2hD} = \frac{1}{2h}\Sigma\theta^2.$$

Again, when the b coefficients are introduced, we have, substituting for α_n in $b_{1n}\alpha_1\alpha_n$, &c.,
$$Q = \frac{1}{\theta_n^2}\left(\frac{d\xi}{dz}\right)^2 + \left(1 + \frac{\theta_1^2}{\theta_n^2} - b_{1n}\frac{\theta_1}{\theta_n}\right)\alpha_1^2 + \&c.$$
$$+ \left(2\frac{\theta_1\theta_2}{\theta_n^2} + b_{12} - b_{1n}\frac{\theta_2}{\theta_n} - b_{2n}\frac{\theta_1}{\theta_n}\right)\alpha_1\alpha_2 + \&c.,$$

and by the same process as before
$$\overline{\left(\frac{d\xi'}{dz}\right)^2} = \partial\,\overline{\left(\frac{d\xi}{dz}\right)^2} = \frac{\partial D_{11}}{2hD} = \kappa\frac{\Sigma\theta^2}{2h} = \kappa\left(\frac{d\xi}{dz}\right)^2.$$

It follows from the above that any form of b which makes
$$\tfrac{1}{2}\Sigma b = -\kappa, \text{ or } \tfrac{1}{2}\int_0^\infty 4\pi r^2\rho b\,dr = -\kappa,$$

and satisfies the equation (33), gives a solution of

$$\left(\frac{d\xi'}{dz}\right)^2 = \kappa\left(\frac{d\xi}{dz}\right)^2,$$

and the solution is independent of the form of the function f, so long as that function satisfies the conditions of Art. 61.

The value of Σb is thus determinate. But the particular form of b which will make $\frac{1}{2}\int_c^\infty 4\pi r^2 \rho b dr = -\kappa$ is not determinate. For instance, let

$$b = -\frac{\mu-3}{3}\frac{c^\mu}{r^\mu}.$$

That is a solution of (33) and (35) for all values of μ greater than 3.

Again, let $$b = -\frac{\mu-3}{\mu}\frac{c^3}{a^3} \text{ when } r < a,$$

$$b = -\frac{\mu-3}{\mu}\frac{c^3}{a^3}\frac{a^\mu}{r^\mu} \text{ when } r > a.$$

That also is a solution for all values of μ greater than 3. Here a may be the radius of a sphere which on average contains one molecule, as in Art. 61.

85. The law of distribution of velocities being ϵ^{-hQ}, where

$$Q = a_1\alpha_1^2 + b_{12}\alpha_1\alpha_2 + a_2\alpha_2^2 + \&c.,$$

let α, β, γ be the velocities of a molecule of mass m, α', β', γ' those of any other molecule. Then, b being small, it is easy to prove that

$$m\Sigma\,(\overline{\alpha\alpha'} + \overline{\beta\beta'} + \overline{\gamma\gamma'}) = -\Sigma\frac{3b}{4h},$$
$$= -T\Sigma b,$$
$$= 2\kappa T,$$

that is, $\frac{1}{2}m\Sigma\,(\overline{\alpha\alpha'} + \overline{\beta\beta'} + \overline{\gamma\gamma'})$ is equal to the Virial (taken as positive) of the intermolecular forces, represented in case of elastic spheres by collisions. In Art. 58, dealing with finite intermolecular forces, we advanced a step further, proving namely that the value of $\frac{1}{2}m\,(\overline{\alpha\alpha'} + \overline{\beta\beta'} + \overline{\gamma\gamma'})$ for any given r is equal to a particular part of the Virial specially related to that value of r. If we are to make a similar step in advance in the case of elastic spheres, it must be by dividing the Virial, if that be possible, into distinct portions, each specially related to a particular r. Instead of the Virial of the definite force which m' exerts on m at distance r, let us calculate the chance that m', so situated, shall be the next sphere to collide with m, multiplied by the mean Virial of that collision if it occurs. That gives us a part of the whole Virial which stands in special relation to r.

Consider a molecule m. The number of collisions between m and m' with relative velocity V in time dt is proportional to $\pi c^2 \rho V dt$. Suppose the whole system to have attributed to it a velocity equal and opposite to that of m for the time being, so as to reduce m to rest. Then the sphere m' which collides with m with relative velocity V must have described a certain free path, which must have commenced at some distance $r \ldots r + dr$ from m.

The chance that it shall have commenced at distance $r \ldots r + dr$ is of the form $q\epsilon^{-qr} dr$, where q is independent of r, but a function of V. But m' starting from collision at distance r from m, is as likely to be moving in any direction as in any other; we must therefore divide ϵ^{-qr} by $4\pi r^2$. Again, the Virial of the collision if it takes place is $\frac{2}{3} m \frac{Vc}{4}$ by Art. 28.

Let us then introducing the factor $\frac{c}{qr^2}$, assume for given V

$$\tfrac{1}{2} b = \frac{\pi c^2 V}{4\pi r^2} \frac{c}{r^2} \epsilon^{-qr} \frac{2}{3} m \frac{Vc}{4},$$

and therefore, given V,

$$\tfrac{1}{2} \Sigma b = \int_c^\infty 4\pi r^2 \rho b \, dr = \frac{2}{3} \pi c^4 \rho \frac{mV^2}{4} \int_c^\infty \frac{1}{r^2} \epsilon^{-qr} dr$$

$$= -\frac{2}{3} \pi c^3 \rho \frac{mV^2}{4},$$

and taking means for all values of V

$$\tfrac{1}{2} \Sigma b = -\tfrac{2}{3} \pi c^3 \rho T = -\kappa T.$$

To express b as a function of r, we must perform the integration according to V, and not according to r. That is

$$\frac{1}{2}b = \frac{2}{3}\frac{\pi c^4}{4\pi r^4}\frac{1}{4}\int_0^\infty C\epsilon^{-\frac{h}{2}V^2 m} V^4 \epsilon^{-qr} dV,$$

in which q is a function of V, and C is the usual constant.

That appears to satisfy all necessary conditions for b. But it is not a complete solution of the problem, because the introduction of the factor $\frac{c}{qr^2}$ is not proved to be necessary, except to satisfy (33). It is possible that, as in Art. 57, the correlation, that is, b, may depend on the angles which the velocities of two molecules make with r, the line joining their positions, as well as on r.

CHAPTER VII.

FINITE INTERMOLECULAR FORCES. BINARY ENCOUNTERS.

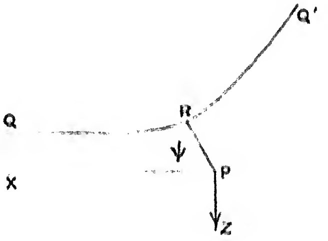
86. It is worth while to apply the method of Chapter v. to molecules between which finite forces act. Nothing is assumed concerning the force acting between two molecules, except (1) that it acts in the line joining their centres, (2) is a continuous function of the distance between their centres, (3) becomes repulsive and infinite as that distance is indefinitely diminished, (4) is evanescent at all distances greater than a certain line c which is very small compared with the dimensions of the space in which the system of molecules is moving. A sphere of radius c described about a molecule shall be called its *sphere of action.*

It seems necessary to assume (3) that for sufficiently small distances the force becomes repulsive and infinite, if we are to hold that there is a very small distance within which two molecules cannot approach each other.

87. With this definition of a molecule, let us assume that the number of molecules scattered through a given space is so small, or the aggregate volume of their spheres of action bears so small a ratio to the space, that no molecule is ever within the sphere of action of more than one other molecule at the same instant. In other words, the encounters are binary. Or that the number of such complex encounters which take place in unit of volume and time bears so small a ratio to the number of binary encounters, that we may without appreciable error assume all the encounters to be binary.

88. Suppose first a molecule P fixed in space. Let PX be any line through P.

Let Q be a point just outside of the sphere of action of P and distant l from PX. And let another particle at Q of mass m move with velocity q parallel to XP. An encounter takes place, and since the encounters are assumed to be binary, m describes a symmetrical curved path QRQ', R being the apse. Let the angle $XPR = \psi$. The whole effect of the encounter, so far as regards the change of direction of the motion of m, is the same as if m received an impulse $2mq \cos \psi$ in direction PR. Then also P experiences an impulse $2mq \cos \psi$ in direction RP.



Let the number per unit of volume of molecules which at or near Q have velocity $q \ldots q + dq$ in direction XP be $f(q)\, dq$. Then the sum of the impulses which P experiences in unit of time from all the molecules which so move is $2mf(q)\, q^2 dq \cos \psi$, and the mean force per unit of time on P due to all molecules moving from Q in direction XP is

$$2m \int f(q)\, q^2 \cos \psi \, dq,$$

ψ being a function of q, and the integration including all values of q. If l also varies ψ is a function of q and l.

Now suppose a circle described about X with radius l in a plane at right angles to XP. Let m, moving parallel to XP, be before encounter anywhere on that circle, and let the angle made by the plane QXP with the plane of the paper be ϵ. R will evidently lie on a circle parallel to the circle described about X.

If PZ be drawn at right angles to PX in the plane of the paper, the mean force on P resolved in direction PZ due to the molecules moving from Q in direction parallel to XP is

$$2m \cos \epsilon \int f(q)\, q^2 \cos \psi \sin \psi dq.$$

And if now l also vary, the mean force on P in direction PZ due to all molecules moving in direction XP, whatever the value of l, is

$$2m \int_0^\pi \cos \epsilon d\epsilon \int_0^\infty 2\pi l dl \int f(q)\, q^2 \cos \psi \sin \psi dq,$$

ψ being now a function of l and q. It is of course zero.

89. If P, instead of being at rest, be moving with velocity u in direction PX, we must write $u+q$ for q in the above expressions. The force on P for any given value of ϵ will then be in direction RP, and equal to

$$2m \int_0^\infty 2\pi l dl \int dq f(q)\, (q+u)^2 \cos \psi.$$

And the mean force on P in direction PZ will be

$$2m \int_0^\pi \cos \epsilon d\epsilon \int_0^\infty 2\pi l dl \int f(q)\, (q+u)^2 \cos \psi \sin \psi dq.$$

Now let the plane of the paper be the plane of XZ, XP the direction of x. Let the function ξ have at P the value ξ_0, and at any point whose z ordinate is ∂z the value $\xi_0 + \frac{d\xi}{dz}\partial z$. Then the velocity of P relative to Q will be $q + u + \frac{d\xi}{dz} l \cos \epsilon$.

And the mean force on P in direction PZ is now

$$4\pi m \int_0^\pi \cos \epsilon d\epsilon \int_0^\infty l dl \int dq f(q) \left(q + u + l \frac{d\xi}{dz} \cos \epsilon\right)^2 \cos \psi \sin \psi.$$

That is, if u, v, w be the component velocities of P,

$$\frac{dw}{dt} = -4\pi m \int_0^\pi \cos \epsilon d\epsilon \int_0^\infty l dl \int dq f(q) \left(q + u + l \frac{d\xi}{dz} \cos \epsilon\right)^2 \cos\psi \sin\psi$$

$$= -4\pi m \int_0^\infty l dl \int dq f(q)\, (q+u)\, l \frac{d\xi}{dz} \cos \psi \sin \psi.$$

And u being negative let us write $-u$ for u. Then

$$u\frac{dw}{dt} = +4\pi m\int_0^\infty ldl\int dqf(q)(qu+u^2)\,l\frac{d\xi}{dz}\cos\psi\sin\psi$$

$$= +4\pi m\int_0^\infty l^2dl\int dqf(q)\,u^2\cos\psi\sin\psi\frac{d\xi}{dz},$$

on average of all values of u; or writing $\frac{1}{2h}$ for $m\overline{u^2}$

$$u\frac{dw}{dt} = \kappa\frac{d\xi}{dz}\frac{1}{2h},$$

where $\kappa = 4\pi\int_0^\infty l^2dl\int dqf(q)\cos\psi\sin\psi.$

By symmetry $w\frac{du}{dt}$ has the same value *mutatis mutandis*,

and therefore $\frac{d}{dt}\overline{uw} = \kappa\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right),$

and $\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)\frac{d}{dt}\overline{uw} = \kappa\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)^2$ ....(36).

90. This agrees in form with the result obtained for elastic spheres in Art. 76. But κ, instead of being a known constant, now depends on the unknown law of force and is a function of $\overline{q^2}$. Further, in the expression for κ, $\cos\psi$ is necessarily positive, because ψ lies between zero and $\frac{\pi}{2}$, and also $\cos\psi\sin\psi$ is necessarily positive, and κ is necessarily positive. Now if $\psi > \frac{\pi}{4}$, $\cos\psi\sin\psi$ diminishes as ψ increases; that is as q increases, because $\frac{d\psi}{dq}$ is positive; if $\psi < \frac{\pi}{4}$, $\cos\psi$ $\sin\psi$ increases as q increases.

Also the condition that ψ shall be less than $\frac{\pi}{4}$ is that l be less than a certain magnitude, which we may call l_0, and the greater q is the smaller must l_0 be. It follows that as $\overline{q^2}$, or the mean kinetic energy, increases, it becomes less probable that ψ shall be less than $\frac{\pi}{4}$, and therefore more probable that $\cos\psi\sin\psi$ shall diminish as q increases.

Therefore if $\overline{q^2}$ be great enough, $\cos\psi \sin\psi$ taken on average of all values of l and q, will ultimately diminish as $\overline{q^2}$ increases. And therefore κ must for sufficiently high values of q^2, that is of the mean kinetic energy, or temperature, if the two are identical, either diminish as the temperature increases, or increase less rapidly than the temperature.

91. We have now to consider the other term in $\frac{dM}{dt}$, namely,

$$\alpha\gamma \frac{d}{dt}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right).$$

Let us again assume the encounters to be binary. As in Art. 68 describe a sphere of radius a about any point O, and let PP' be a double ordinate parallel to z, P and P' being on the surface of the sphere.

Then $$\frac{\overline{d\xi}}{dz} = \iint dxdy\,(\xi_P - \xi_{P'}) \div \frac{4\pi a^3}{3}.$$

Suppose two molecules to encounter one another, the point of contact of their spheres of action being at the centre of the sphere. Let V_x, V_y, V_z be the components of their relative velocity before encounter. We may suppose their common centre of inertia at rest, since its motion will not affect ξ_P on average.

Let us consider the change of $\frac{\overline{d\xi}}{dz}$ due to this encounter only, that is

$$\iint dxdy\left(\frac{d\xi_P}{dt} - \frac{d\xi_{P'}}{dt}\right) \div \frac{4\pi a^3}{3}.$$

First to find $\frac{d\xi_P}{dt}$, let f be referred to P as centre, and let f_0 denote its value at the centre of inertia of the two spheres of action. Let f be the value of f at the centre of either sphere when the encounter begins. After the encounter has ceased f will have become f', corresponding to the final relative position of the two spheres of action. Let V_x, V_z have become V_x', V_z'.

If $\partial\xi_p$ be the change in ξ_p due to the encounter, $\partial\xi_p$ is, omitting the factor $\frac{1}{\Sigma f}$ which is on average constant, proportional to, and has the same sign as

$$V_x'f' - V_x f,$$

that is, if we write $V_x = \lambda V$, $V_x' = \lambda' V$, &c., the same sign as $\lambda' f' - \lambda f$.

Now let θ be the angle between the relative velocity, whose direction cosines are λ, μ, ν, and the line of centres at the commencement of encounter.

Then $2\psi - \theta$ is the corresponding angle at the end of the encounter, ψ being the angle so denoted in Art. 88.

Then we have, $\frac{c}{2}$ being the radius of the sphere of action,

$$f = f_0 + \frac{c}{2}\left(-\nu\cos\theta + \sqrt{1-\nu^2}\sin\theta\cos\phi\right)\frac{df}{dz},$$

$$f' = f_0 + \frac{c}{2}\left(-\nu\cos\overline{2\psi-\theta} + \sqrt{1-\nu^2}\sin\overline{2\psi-\theta}\cos\phi\right)\frac{df}{dz};$$

also as shown in Art. 72,

$$\lambda' = -\lambda\cos 2\psi - \frac{\lambda\nu}{\sqrt{1-\nu^2}}\sin 2\psi\cos\phi,$$

and therefore, omitting $\cos\phi$ and writing $\frac{1}{2}\pi$ for $\cos^2\phi$ as the result of integrating according to ϕ,

$$\lambda' f' = \lambda' f_0 + \frac{c}{2}\lambda\nu\,.\left(\cos 2\psi\cos\overline{2\psi-\theta} - \tfrac{1}{2}\sin 2\psi\sin\overline{2\psi-\theta}\right)\frac{df}{dz}$$

$$\begin{aligned} &= \lambda' f_0 + \frac{c}{2}\lambda\nu\,.\,\frac{df}{dz}\{\cos\theta\,(4\cos^4\psi - 4\cos^2\psi + 1) \\ &\qquad - \cos\theta\; 2\cos^2\psi\sin^2\psi \\ &\qquad + \sin\theta\; 2\sin\psi\cos\psi\,(2\cos^2\psi - 1) \\ &\qquad + \sin\theta\sin\psi\cos\psi\,(2\cos^2\psi - 1)\}. \end{aligned}$$

Also

$$\lambda f = \lambda f_0 + \lambda \frac{c}{2}(-\nu\cos\theta + \sqrt{1-\nu^2}\sin\theta\cos\phi)\frac{df}{dz}$$

$$= \lambda f_0 - \lambda\nu\frac{c}{2}\cos\theta\frac{df}{dz},$$

on average. Also for the pair of spheres $(\lambda' - \lambda)f_0 = 0$, and

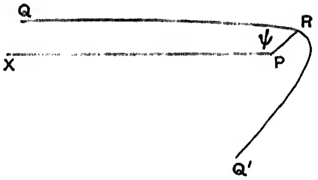
$$\int_0^{\frac{1}{2}\pi} 2\cos\theta\sin\theta\, d\theta\,(\lambda' f' - \lambda f)$$

$$= \lambda\nu\frac{c}{2}\frac{df}{dz}\int_0^{\frac{1}{2}\pi} 2\cos^2\theta\sin\theta\, d\theta\,(6\cos^4\psi - 6\cos^2\psi + 2)$$

$$+ \lambda\nu\frac{c}{2}\frac{df}{dz}\int_0^{\frac{1}{2}\pi} 2\sin^2\theta\cos\theta\, d\theta\, 3\sin\psi\cos\psi(2\cos^2\psi - 1)\ldots(36),$$

which can be easily shown to be positive, θ being less than ψ, and ψ less than $\frac{1}{2}\pi$. Therefore $\alpha\gamma\frac{d}{dt}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)$ is positive.

92. If instead of being repulsive as hitherto assumed, the force between the molecules P and m be attractive, it is possible that the approach of the two may result in a permanent union, each molecule revolving in a closed curve round the common centre of inertia. Leaving this case out of consideration, the form of the path described by m with reference to P regarded as fixed will for attractive force be as in this figure.



The angle ψ is now between $\frac{\pi}{2}$ and π instead of between zero and $\frac{\pi}{2}$ as in the case of the repulsive force. The impulse on m is represented as before by $2mq\cos\psi$, $\cos\psi$ being now negative. The mean force on P due to a succession of encounters is in direction PR instead of RP. The reasoning of Art. 89 will apply equally well to this case, except that in the result $u\frac{dw}{dt}$ will be of the opposite sign to $\frac{d\xi}{dz}$ instead of the same sign, and $\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)\frac{d}{dt}uw$ will be negative.

That leads in stationary motion to a positive sign for the coefficients b. It is conceivable that the force between two molecules, being a function of the distance r between them, may change sign at some value of r. If however there be a limit of distance within which the centres of inertia of two molecules cannot approach each other, the force must ultimately, as r is indefinitely diminished, become repulsive. And as the density increases the near approaches becoming more frequent, the repulsive forces must ultimately predominate. The effect of the attractive forces, if such exist, will be, not to make the b's positive, but to make them have less negative value than they otherwise would have.

93. So far we have assumed the encounters to be binary, so that for each encounter either molecule describes a complete symmetrical orbit with reference to the other, complete that is in the sense that after the two have separated to the very small distance c from each other, the motion of either is sensibly rectilinear in the asymptote. If we remove the restriction to binary encounters, we may reason as follows.

Assume $\frac{d\xi}{dz}$ to be positive at the origin P. Then a molecule at P moving with u negative has greater velocity relative to molecules on the side of positive z than to those on the side of negative z. On the average therefore the potential of the mutual action of P and the other molecules will be greater with z positive than with z negative. Let p be that potential. Then $\frac{dp}{dz}$ is positive.

Therefore if u, v, w be the component velocities of P, $\frac{dw}{dt}=-\frac{dp}{dz}$ is on average negative. And therefore $u\frac{dw}{dt}$ is on average positive, or has the same sign with $\frac{d\xi}{dz}$. Also its sign has no relation to $\frac{d\zeta}{dx}$.

Similarly $w\frac{du}{dt}$ is on average of the same sign as $\frac{d\zeta}{dx}$, and independent of the sign of $\frac{d\xi}{dz}$. And therefore

$$\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)\frac{d}{dt}\overline{uw}=\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)\left(u\frac{dw}{dt}+w\frac{du}{dt}\right)$$

is necessarily positive.

And therefore in a system of molecules of the kind now considered $\frac{dM}{dt}$ is positive, and the motion not stationary if ξ^2, η^2, ζ^2 of Art. 61 have the same mean values as they would have in the medium of material points. To effect stationary motion, ξ^2, η^2, ζ^2 must be increased as we found to be the case with elastic spheres.

CHAPTER VIII.

GENERAL THEORY OF THE STATIONARY MOTION.

94. HAVING established the results contained in Chapters IV. and V., I shall now assume for the law of distribution of the coordinates and velocities among an infinite number of molecules in stationary motion the following, namely: The chance that at any instant the coordinates of the molecules, n in number, shall lie respectively between the limits

$$\begin{array}{ccc} x_1 & \text{and} & x_1+dx_1, \\ y_1 & ,, & y_1+dy_1, \\ z_1 & ,, & z_1+dz_1, \\ \multicolumn{3}{c}{\cdots\cdots\cdots\cdots} \\ x_n & \text{and} & x_n+dx_n, \\ y_n & ,, & y_n+dy_n, \\ z_n & ,, & z_n+dz_n, \end{array}$$

and their component velocities between the limits

$$\begin{array}{ccc} \alpha_1 & \text{and} & \alpha_1+d\alpha_1, \\ \beta_1 & ,, & \beta_1+d\beta_1, \\ \gamma_1 & ,, & \gamma_1+d\gamma_1, \\ \multicolumn{3}{c}{\cdots\cdots\cdots\cdots} \\ \alpha_n & \text{and} & \alpha_n+d\alpha_n, \\ \beta_n & ,, & \beta_n+d\beta_n, \\ \gamma_n & ,, & \gamma_n+d\gamma_n, \end{array}$$

is $$\left(\frac{h}{\pi}\right)^{\frac{n}{2}} \sqrt{D} A \epsilon^{-hQ}\, dx_1 \ldots dz_n d\alpha_1 \ldots d\gamma_n.$$

Here $$Q = a_1(\alpha_1^2 + \beta_1^2 + \gamma_1^2) + a_2(\alpha_2^2 + \beta_2^2 + \gamma_2^2) + \&c.$$
$$+ b_{12}(\alpha_1\alpha_2 + \beta_1\beta_2 + \gamma_1\gamma_2) + \&c.$$

The 'a' coefficients are independent of the positions of the molecules. Every b, as b_{pq}, is a function of the distance, r_{pq}, at the instant in question between the molecules to whose velocities the suffixes pq relate, such functions satisfying the conditions of Chap. V. D is the determinant of the coefficients in Q.

Again, A may be explicitly a function of the coordinates x, y, z, &c., or may be a constant, $\sqrt{D}$ is a function of the coordinates, only as contained in the coefficients b. Then evidently

$$\left(\frac{h}{\pi}\right)^{\frac{n}{2}} \sqrt{D} \iiint \dots \epsilon^{-hQ}\, d\alpha_1 \dots d\gamma_n = 1.$$

Instead of using the word *chance*, we may say that the above expression represents the *time* during which on the average of any very long time the coordinates and component velocities will be found respectively within the limits aforesaid.

95. The function Q may conveniently be put in the form

$$Q = a_1\alpha_1^2 + \tfrac{1}{2}b_{12}\alpha_1\alpha_2 + \tfrac{1}{2}b_{13}\alpha_1\alpha_3 + \&c.$$
$$+ a_2\alpha_2^2 + \tfrac{1}{2}b_{21}\alpha_2\alpha_1 + \tfrac{1}{2}b_{23}\alpha_2\alpha_3 + \&c.$$
$$+ \&c.,$$

in which each line is appropriated to a particular molecule.

96. According to the results obtained in Chapters IV.—VI. it is necessary for stationary motion that $\overline{\xi'^2} + \overline{\eta'^2} + \overline{\zeta'^2}$ (Art. 79) shall have a certain value. That necessary value it will have if suitable values be given to the coefficients b as functions of r. The coefficients b being so determined, the motion is stationary, so far as not to be disturbed by the collisions or mutual forces of the molecules. I assume now that in Q the b coefficients have the values so determined.

97. We can now deduce the fundamental property of this distribution, namely, that for any given set of positions of the molecules, or as we shall call it, for any given configuration,

$$\alpha_1 \frac{dQ}{d\alpha_1} = \alpha_2 \frac{dQ}{d\alpha_2} = \&\text{c., on average.}$$

For
$$\frac{dQ}{d\alpha_1} = 2a_1\alpha_1 + b_{12}\alpha_2 + b_{13}\alpha_3 + \&\text{c.}$$

If, with α_1 constant, α_2, α_3 &c., assume all possible values consistent with the conservation of energy, we find (see Appendix (*h*)) that the mean value of

$$\frac{dQ}{d\alpha_1}, \text{ or } 2a_1\alpha_1 + b_{12}\alpha_2 + \&\text{c.},$$

is $\frac{D}{D_{11}}\alpha_1$, D being the determinant of the coefficients a, b, &c. in Q, and D_{11} its coaxial minor obtained by striking out the row and column containing α_1. Therefore also

$$\alpha_1 \frac{dQ}{d\alpha_1} = \frac{D}{D_{11}} \alpha_1^2 \text{ on average.}$$

But it is also shown (Appendix (*g*)) that

$$\overline{\alpha_1^2} = \frac{D_{11}}{hD},$$

whence on average

$$\overline{\alpha_1 \frac{dQ}{d\alpha_1}} = \frac{D}{D_{11}} \frac{D_{11}}{hD} = \frac{1}{h}.$$

Similarly
$$\overline{\alpha_2 \frac{dQ}{d\alpha_2}} = \frac{1}{h} \;\&\text{c.}$$

and
$$\overline{\alpha_1 \frac{dQ}{d\alpha_1}} = \overline{\alpha_2 \frac{dQ}{d\alpha_2}} = \&\text{c.} \qquad \text{I.}$$

98. Inasmuch as the system is infinite, and there is no direct action between any molecule and any other molecule except at distances very small compared with the dimensions of the system, not only is the sum of the potential and kinetic energies constant, but the kinetic energy of the whole system is itself separately constant. Let the kinetic energy be

$$T = \tfrac{1}{2} m_1 (\alpha_1^2 + \beta_1^2 + \gamma_1^2) + \tfrac{1}{2} m_2 (\alpha_2^2 + \beta_2^2 + \gamma_2^2) + \&\text{c.}$$

Here if α_1 be velocity of translation m is mass, if α be velocity of rotation m denotes moment of inertia, and so on. Then we have by the constancy of T,

$$m_1\alpha_1\frac{d\alpha_1}{dt}+m_2\alpha_2\frac{d\alpha_2}{dt}+\&c.=0 \quad \ldots\ldots\ldots\ldots\ldots \text{II.}$$

For the same reason Q is separately constant, or

$$\frac{dQ}{d\alpha_1}\frac{d\alpha_1}{dt}+\frac{dQ}{d\alpha_2}\frac{d\alpha_2}{dt}+\&c.=0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{III.}$$

Now II. and III. suggest the inference

$$\frac{dQ}{d\alpha_1}\Big/ m_1\alpha_1=\frac{dQ}{d\alpha_2}\Big/ m_2\alpha_2=\&c. \quad \ldots\ldots\ldots\ldots\ldots \text{IV.}$$

An obvious solution of this is $Q=\frac{1}{2}\Sigma m(\alpha^2+\beta^2+\gamma^2)$. But, as proved in Chapters IV. and V., this does not give stationary motion when the molecules have finite dimensions, except in the limiting case of infinite rarity.

99. Concerning the *Maxwell-Boltzmann Law*

$$m_1\overline{\alpha_1^2}=m_2\overline{\alpha_2^2}=\&c.$$

This follows at once from Art. 97, and IV., if IV. be accepted. It must however be noted that IV., although a consistent, is not a necessary, consequence of II. and III. For while α_1, α_2, &c. are unchanged, let all the molecules undergo small displacements. Then $\frac{d\alpha_1}{dt}$, $\frac{d\alpha_2}{dt}$ &c., depending as they do on the intermolecular forces, will receive variations, which may be arbitrary, as the displacements are arbitrary. If under these circumstances $\frac{dQ}{d\alpha_1}$, &c. remained unchanged, IV. would be a necessary consequence of II. and III. But $\frac{dQ}{d\alpha_1}$ &c. do not remain unchanged. So IV. is not proved by II. and III.

If we assume condition A, we assume in effect that the b coefficients are all zero, and $Q=\Sigma m\alpha^2$. It follows then at once from the law of distribution ϵ^{-hQ} that $m_1\overline{\alpha_1^2}=m_2\overline{\alpha_2^2}=\&c.$ The law is therefore true whenever condition A can legitimately be assumed. It is true, that is, in the limiting case of infinite rarity.

I am not aware that it has ever been proved in any other case, or by any assumption not equivalent to condition A.

If it were true in the general case, we should have, comparing II. with III.,

$$\frac{dQ}{d\alpha_1}\bigg/ m_1\alpha_1 = \frac{dQ}{d\alpha_2}\bigg/ m_2\alpha_2 = \&c.,$$

and therefore by Art. 97,

$$\frac{D}{m_1D_{11}} = \frac{D}{m_2D_{22}} = \&c.$$

or

$$m_1D_{11} = m_2D_{22} = \&c.$$

But D_{11} D_{22}, &c. are functions, not only of the masses of the molecules m_1 m_2, &c., but (if they be elastic spheres) also of their diameters, (if they be centres of force) of their effective volumes. It seems therefore to follow that the law

$$m_1\alpha_1^2 = m_2\alpha_2^2, \ \&c.$$

cannot hold universally. It can be accepted only on the authority of the great physicists by whose name it is known.

100. If therefore we write

$$\frac{dQ}{d\alpha_1}\bigg/ m_1 = \mu_1\alpha_1,$$

$$\frac{dQ}{d\alpha_2}\bigg/ m_2 = \mu_2\alpha_2, \ \&c.,$$

μ_1, μ_2, &c. will in general have different values for different kinds of molecules in our system. Only in the case where the molecules are all of the same kind, may we write $\frac{dQ}{d\alpha}\Big/ m = \mu\alpha$, where μ is constant.

In all cases however in which the b coefficients are very small μ_1, μ_2, &c. will be very approximately equal to each other. For in the limiting case when the b's are all zero

$$Q = a_1\alpha_1^2 + a_2\alpha_2^2 + \&c.,$$

and we know that $a_1 = m_1$, $a_2 = m_2$, &c. When the b's are not zero, every coaxial minor, as D_{11}, consists of the product of all the axial constituents $m_2m_3 \ldots$, and of other terms each of which contains the product of not less than two b's. The quantities $m_1\alpha_1^2$, $m_2\alpha_2^2$, &c. will therefore, as long as the b's are small, differ from each other only by small quantities of the second order.

Field of external force.

101. We may now equate to zero the time differential of $A\sqrt{D}\epsilon^{-hQ}$, and so obtain, applying Boltzmann's general method,

$$\Sigma\left(\frac{dx}{dt}\frac{d}{dx}+\frac{dy}{dt}\frac{d}{dy}+\frac{dz}{dt}\frac{d}{dz}\right)A\sqrt{D}\epsilon^{-hQ}$$

$$+\Sigma\left(\frac{d\alpha}{dt}\frac{d}{d\alpha}+\frac{d\beta}{dt}\frac{d}{d\beta}+\frac{d\gamma}{dt}\frac{d}{d\gamma}\right)A\sqrt{D}\epsilon^{-hQ}=0.$$

But $$\frac{dx}{dt}=\alpha,\quad \frac{dy}{dt}=\beta,\quad \frac{dz}{dt}=\gamma.$$

Again let the forces acting on the system have a potential χ. Then

$$m_1\frac{d\alpha_1}{dt}=-\frac{d\chi}{dx_1},$$

$$m_2\frac{d\alpha_2}{dt}=-\frac{d\chi}{dx_2},\ \&c.$$

And the equation becomes, arranging the terms,

$$\sqrt{D}\,\Sigma\left(\alpha\frac{dA}{dx}-\frac{hA}{m}\frac{d\chi}{dx}\frac{dQ}{d\alpha}\right)+\sqrt{D}\,\Sigma\left(\beta\frac{dA}{dy}-\frac{hA}{m}\frac{d\chi}{dy}\frac{dQ}{d\beta}\right)$$

$$+\sqrt{D}\,\Sigma\left(\gamma\frac{dA}{dz}-\frac{hA}{m}\frac{d\chi}{dz}\frac{dQ}{d\gamma}\right)$$

$$+A\frac{1}{2\sqrt{D}}\Sigma\Sigma\alpha\frac{dD}{db}\frac{db}{dx}+\&c.$$

$$-Ah\sqrt{D}\,\Sigma\Sigma(\alpha\alpha'+\beta\beta'+\gamma\gamma')\left(\alpha\frac{db}{dx}+\beta\frac{db}{dy}+\gamma\frac{db}{dz}\right)=0.$$

Let us first consider the terms which involve differentiation of the b's. Since every b is a function of the corresponding r, and of that alone,

$$\frac{db}{dx}=\frac{db}{dr}\frac{dr}{dx}=\frac{db}{dr}\frac{x-x'}{r}\ \&c.,$$

where $$r^2=(x-x')^2+(y-y')^2+(z-z')^2.$$

Therefore
$$\Sigma\Sigma\alpha\frac{dD}{db}\frac{db}{dx}=\Sigma\Sigma\alpha\frac{dD}{db}\frac{db}{dr}\frac{dr}{dx}$$

$$=\alpha_1\frac{dD}{db_{12}}\frac{db_{12}}{dr_{12}}\frac{x_1-x_2}{r_{12}}+\alpha_1\frac{dD}{db_{13}}\frac{db_{13}}{dr_{13}}\frac{x_1-x_3}{r_{13}}+\&\text{c.}$$

$$-\alpha_2\frac{dD}{db_{12}}\frac{db_{12}}{dr_{12}}\frac{x_1-x_2}{r_{12}}-\&\text{c.},$$

because
$$\frac{dr_{12}}{dx_1}=-\frac{dr_{12}}{dx_2}\ \&\text{c.}$$

The above expression can by taking the terms in pairs be resolved into a series of terms of the form

$$\frac{dD}{db}\frac{db}{dr}\frac{(\alpha-\alpha')(x-x')}{r},$$

and is therefore zero on average.

Similarly

$$\Sigma\Sigma(\alpha\alpha'+\beta\beta'+\gamma\gamma')\left(\alpha\frac{db}{dx}+\beta\frac{db}{dy}+\gamma\frac{db}{dz}\right)$$

can be resolved into a series of terms of the form

$$(\alpha\alpha'+\beta\beta'+\gamma\gamma')\frac{db}{dr}\frac{(\alpha-\alpha')(x-x')}{r},$$

and is therefore also zero on average.

102. We have then

$$\sqrt{D}\Sigma\left(\alpha\frac{dA}{dx}-\frac{hA}{m}\frac{d\chi}{dx}\frac{dQ}{d\alpha}\right)$$
$$+\&\text{c.}=0,$$

or dividing by A,

$$\left(\alpha_1\frac{d\log A}{dx_1}-\frac{h}{m_1}\frac{d\chi}{dx_1}\frac{dQ}{d\alpha_1}\right)+\left(\alpha_2\frac{d\log A}{dx_2}-\frac{h}{m_2}\frac{d\chi}{dx_2}\frac{dQ}{d\alpha_2}\right)+\&\text{c.}=0.$$

And taking mean values of $\frac{dQ}{d\alpha}$ from Art. 97,

$$\alpha_1\left(\frac{d\log A}{dx_1}-h\frac{d\chi}{dx_1}\frac{D}{m_1D_{11}}\right)+\alpha_2\left(\frac{d\log A}{dx_2}-h\frac{d\chi}{dx_2}\frac{D}{m_2D_{22}}\right)+\&\text{c.}=0.$$

And since
$$\frac{D}{m_1 D_{11}} = \frac{D}{m_2 D_{22}} = \&c. = \mu,$$

$$\alpha_1 \left(\frac{d \log A}{dx} - h \frac{d\chi}{dx_1} . \mu \right) + \alpha_2 \left(\frac{d \log A}{dx_2} - h \frac{d\chi}{dx_2} \mu \right) + \&c. = 0.$$

This is satisfied by assuming, if the molecules be all of the same kind,
$$A = \epsilon^{-h\mu\chi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (37).$$

We have then for the law of distribution of coordinates and velocities in a field of external force whose potential is χ

$$\left(\frac{h}{\pi}\right)^{\frac{n}{2}} \sqrt{D}\, \epsilon^{-h\mu\chi}\, \epsilon^{-hQ}\, dx_1 \ldots dz_n d\alpha_1 \ldots d\gamma_n \ldots\ldots (38).$$

Now
$$\overline{m_1 \alpha_1^2} = \frac{m_1 D_{11}}{hD} = \frac{1}{h\mu}$$

and
$$nT = \tfrac{1}{2} \Sigma m \left(\alpha^2 + \beta^2 + \gamma^2\right) = \frac{3n}{2h\mu},$$

the system consisting of n molecules of the same kind.

But
$$\bar{Q} = a_1 \overline{\alpha_1^2} + b_{12} \overline{\alpha_1 \alpha_2} + \&c.$$
$$= \frac{a_1 D_{11} + b_{12} D_{12} + a_2 D_{22} + \&c.}{hD}$$
$$= \frac{3n}{2h}.$$

Therefore
$$\bar{Q} = \mu n T \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (39).$$

103. With regard to the inclusion of the intermolecular forces under the potential χ the same considerations apply as in Chap. III. I shall assume that we may use the form $\epsilon^{-h(\chi+\psi)}$.

As an example let us now again consider the system of equal elastic spheres in vertical column, Arts. 29 and 45. In that case χ is the potential of the constant vertical force. Let us suppose κ, and therefore all the b coefficients, very small. If the x velocity of any molecule, as u_1, be given, the mean value of u_2 is $-\frac{D_{12}}{D_{11}}u_1$, where D is the determinant

$$D = \begin{vmatrix} 2 & b_{12} & b_{13}\dots \\ b_{12} & 2 & b_{23}\dots \\ \dots & \dots & \dots \end{vmatrix}$$

for in this case the a coefficients may each be replaced by unity.

Now D_{12} contains the term $-b_{12}$ multiplied by axial coefficients only, and other terms each of which contains the product of at least two b's. Therefore if each b be small enough, the mean value of u_2 is ultimately $-\frac{1}{2}b_{12}u_1$.

Similarly $$\overline{u}_3 = -\tfrac{1}{2}b_{13}u_1, \text{ \&c.,}$$

and therefore $$\frac{\overline{dQ}}{du_1} = \mu m_1 u_1 = (2 - \tfrac{1}{2}\Sigma b^2)\,u_1,$$

or $$m_1\mu = (2 - \tfrac{1}{2}\Sigma b^2).$$

It thus appears that $\epsilon^{-h\mu\chi}$ differs from $\epsilon^{-2h\chi}$, when κ is small, only by small quantities of the second order. Now the factor $\epsilon^{-(\kappa-\kappa_0)}$, or $\epsilon^{-\kappa}$, in the expression for the density in Art. 29 corresponds, not to $\epsilon^{-h\mu\chi}$, but to $\epsilon^{-2h\psi}$. That is, if ψ be the potential of the intermolecular forces, $\epsilon^{-\kappa}$ is what $\epsilon^{-2h\psi}$ or $\epsilon^{-h\mu\psi}$ becomes in the limit when the forces become infinite for the distance $r = c$.

And κ being small the solution agrees with that of Art. 29. It does not however agree with that of Art. 29 when κ^2, &c. cannot be neglected. Which result then are we to accept in this case? Evidently the result $\epsilon^{-h\mu\chi}$, because Art. 29 is based on the *tacit* assumption of condition A, and therefore holds only for small values of κ. To sum up the discussions of this problem.

If κ be neglected, the law of density is $\epsilon^{-2h\chi}$, with $T = \frac{3}{4h}$.

If κ^2, &c., but not κ, be neglected, the law is $\epsilon^{-2h\chi}\epsilon^{-\kappa}$, with

$$T = \frac{3}{4h}.$$

If κ^2, &c., are not to be neglected, the law is $\epsilon^{-h\mu\chi}\epsilon^{-\kappa}$, with

$$T = \frac{3}{4\mu h}.$$

Boltzmann's Minimum function.

104. The following theorem is not to be compared in elegance with the theorem founded on condition A, Art. 38, but has the advantage that condition A is not assumed.

Let $f(u_1 \dots u_n x_1 \dots z_n)$, or f, be any positive function of the coordinates $x_1 \dots z_n$, and velocities $u_1 \dots u_n$, of a system of molecules, and of certain parameters a, b, &c. Let ∂f be a small variation of f, a, b, &c., being constant. Let us write $f + \partial f = f\overline{1+q}$, or $\partial f = qf$.

Let the variation ∂f, or qf, be made subject to the following conditions, viz.

$$\iint \dots f\overline{1+q}\, dx_1 \dots dz_n du_1 \dots du_n$$

$$= \iint \dots f dx_1 \dots dz_n du_1 \dots du_n,$$

or writing $dsd\sigma$ for the continued product of differentials,

$$\iint \dots fq dsd\sigma = 0 \quad \dots\dots\dots\dots\dots\dots\dots (1).$$

Also
$$\iint \dots f\overline{1+q}\, C dsd\sigma = \iint \dots f C dsd\sigma,$$

or
$$\iint \dots fq C dsd\sigma = 0 \quad \dots\dots\dots\dots\dots\dots\dots (2),$$

where C is any function the constancy of which is prescribed.

Again, let

$$H = \iint \dots f(\log f - 1)\, dsd\sigma,$$

$$H + \partial H = \iint \dots f\overline{1+q}\, \{\log (f\overline{1+q}) - 1\}\, dsd\sigma.$$

We have then

$$\begin{aligned}
H+\partial H &= \iint\cdots f(\log f-1)\,dsd\sigma \\
&\quad+\iint\cdots f\log\overline{1+q}\,dsd\sigma \\
&\quad+\iint\cdots fq\log f\,dsd\sigma \\
&\quad+\iint\cdots fq\log\overline{1+q}\,dsd\sigma \\
&\quad-\iint\cdots fq\,dsd\sigma \\
&= H+\iint\cdots f\frac{q^2}{2}\,dsd\sigma \\
&\quad+\iint\cdots f\left(q^2-\frac{q^3}{2}\right)dsd\sigma \\
&\quad+\iint\cdots fq\log f\,dsd\sigma \\
&= H+\tfrac{1}{2}\iint\cdots fq^2\,dsd\sigma \\
&\quad+\iint\cdots fq\log f\,dsd\sigma,
\end{aligned}$$

because q^3 is to be neglected.

In order that ∂H may be necessarily positive, or H may be least possible, subject to (1) and (2), it is necessary, and it is sufficient that $\iint fq\log f\,dsd\sigma=0$, that is by (2) that $\log f$ shall be a function of C, that is that $f=A\epsilon^{-hC}$, where

$$\iint\cdots fC\,dsd\sigma$$

is constant.

We may write $\left(\frac{h}{\pi}\right)^{\frac{n}{2}}A\sqrt{D}$ for A and Q for C. The actual value of H when minimum is

$$\frac{n}{2}\log\frac{h}{\pi}+\log A+\frac{1}{2}\log D-\frac{3n}{2}\text{............}(40).$$

Physical effect of the b coefficients.

105. From the law of distribution at which we have now arrived we can find the mean value of any of the products of the form $\alpha\alpha'$, &c. For instance, $\overline{\alpha_1\alpha_2} = D_{12}/hD$, D being the determinant of the coefficients. And all the b's being negative, D_{12} is necessarily positive. If we have only two variables x and y, and if

$$Q = ax^2 + bxy + cy^2,$$

b being negative, we find $D_{12} = -b$, which is positive.

So with three variables, x, y, z, and

$$\begin{aligned} Q &= a_1x^2 + a_2y^2 + a_3z^2 \\ &\quad + b_{12}xy + b_{13}xz + b_{23}yz, \end{aligned}$$

we find
$$D_{12} = -2a_3b_{12} + b_{13}b_{23},$$

which, every b being negative, is positive. (See Appendix (b) as to the sign of these minors.)

The conclusion to be drawn from this is that if two molecules are so near each other that b is not negligible, they are on average moving in the same direction. There is at every point on average a determinate energy of stream motion. It follows further from this uniformity of direction that if $\overline{\alpha\beta}$, $\overline{\alpha\gamma}$, $\overline{\beta\gamma}$, be the mean values of those functions for all molecules within any small finite space, $(\overline{\alpha\beta})^2$, &c. have greater value than they would have if the molecules were material points.

Another consequence of the b coefficients.

106. But we might also, treating the velocities as constants, proceed as follows.

Let for a moment the chance that two molecules distant r from each other shall have velocities in x, $u \dots u + du$ and $u' \dots u' + du'$ be proportional to

$$\epsilon^{-h(u^2 - buu' + u'^2)}\,du\,du',$$

in which b may be $q\dfrac{c^n}{r^n}$, and $n > 3$.

It is convenient here to treat b as positive, and prefix to it the minus sign in the index. That being the case, if b be not negligible, that is if r be small, uu' is more likely to be positive than negative. If r be great, and therefore b negligible, it is indifferent. It follows by the theory of inverse probabilities that, it being given that uu' is positive, r is more likely to be small than if nothing were known of the sign of uu'. If on the other hand it be given that uu' is negative, r is less likely to be small.

Suppose a molecule at P with velocity u, and an element of volume $d\omega$ at P', distant r from P. Let the chance that there shall be within $d\omega$ a molecule moving with velocity u' be $\psi d\omega$, when PP', or r, is great, and $b=0$. Then when $b \neq 0$, the chance becomes

$$\psi d\omega \epsilon^{huu'b},$$

which is greater or less than $\psi d\omega$, according as uu' is positive or negative.

Further, the chance that there shall be a molecule within $d\omega$ with velocity either u' or $-u'$ is, since *a priori* $+u'$ and $-u'$ are equally probable, and the system is supposed infinite,

$$\tfrac{1}{2}\psi d\omega\,(\epsilon^{huu'b} + \epsilon^{-huu'b}),$$

uu' being now treated as essentially positive. That expression is equal to $\psi d\omega$ if b^2 and higher powers of b are neglected. But if b^2, &c. be taken into account, it is greater than $\psi d\omega$.

107. It follows from this result that under the law of distribution of coordinates and velocities at which we have arrived in this chapter, if at any instant we calculated for each of the molecules the value of Σb, or the sum of the b coefficients connecting the u velocities of that molecule with the velocities of each of the others, the average value of Σb would be greater than it would be were all the molecules scattered through space at random. That signifies that the molecules of the entire system would be collected into denser and rarer masses—the effect of which evidently is to increase the mean value of Σb for all molecules. Further the ratio $\overline{\xi'^2} : \xi^2$ would have a greater value for the denser masses than for the rarer ones, or the stream motion would be greater for the denser masses than for the rarer ones. So that the system would tend more and more, with increasing number of molecules in a given space, to assume the form of a number of denser aggregates, say clouds, moving through a comparatively rare medium.

108. It is not essential to my argument, but I will here give what appears to me the best possible definition of density at a given point at a given instant, for molecules of finite dimensions.

I would define namely as follows. The density at any point P at any instant is $-\Sigma b$, where Σb is the sum of the b coefficients, all being negative, of all the molecules of the system referred to the point P—that is, b for any molecule is a function of the distance of that molecule from P.

109. It is assumed throughout this investigation that the quadratic function Q is positive, that is, that the coefficients a, b, are such that Q cannot be made negative, whatever values we assign to the velocities. It is assumed that the distribution of the molecules in space, and therefore the coefficients b, are on the average such as would be calculated by the method above indicated, the whole number of molecules of the system in a given finite space, *i.e.* ρ, being known. Should that condition ever fail, the motion of the system can no longer be represented by the law considered in this chapter. It is reasonable to expect that the change of the mathematical formulæ will coincide with a change in the physical state of the system.

110. The condition that Q shall be necessarily positive, whatever values be assigned to the velocities, is that the determinant D, of the coefficients in Q and all its coaxial minors must be positive. See Appendix (p). As the b coefficients increase in absolute magnitude, D, being positive, diminishes. But as the density ρ increases *cœteris paribus*, the b coefficients do generally increase in absolute magnitude, and D, with all its coaxial minors, generally diminishes. The b coefficients are generally also functions of the mean kinetic energy, or temperature, as well as of the density, and if the temperature be high enough, probably diminish as that increases (Art. 90). As the density increases, or temperature diminishes, or both, the system may ultimately arrive at a state, in which *D* or some of its coaxial minors becomes zero or negative, and then the change of physical state ensues, whatever its true description be. Now to any group of molecules we choose to select, and therefore to all the molecules forming one of the denser masses or clouds above mentioned, belongs a particular coaxial minor, that namely obtained by striking out all the axial constituents of *D* except those which belong to molecules of the group. Generally therefore the condition may be expected to fail for some of these coaxial minors before it fails for the complete determinant *D*. So that as density and temperature vary continuously, the change of state, or liquefaction if such it be, will take place partially and gradually, some portions of the system having passed into the changed state, while other portions remain in the original state. Further, the higher the temperature, at all events after a certain point is reached, the greater the condensation necessary to make *D*, or any coaxial minor vanish, and therefore to produce the physical change in question.

Such is the process which our analysis leads us to expect. Physicists may consider how far it corresponds with what is known to take place in gases under condensation, or on what (if any) farther hypothesis it may be made to correspond with it.

CHAPTER IX.

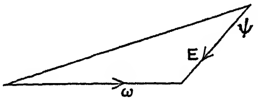
OF MOLECULES AS CARRIERS.

111. THE molecules being elastic spheres, and condition A being assumed, to find the mean free path for a sphere issuing from collision with velocity ω. As the mean free path has received more than one definition, I define it as follows. Suppose a sphere m to start from a collision with velocity ω, and to undergo n successive collisions. After each collision let each of the colliding molecules have restored to it the velocity which it had before collision. Then our sphere will describe n paths $l_1, l_2 \dots l_n$ between its collisions, each with the same velocity ω. The mean free path for velocity ω is then

$$\lambda_\omega = \frac{l_1 + l_2 + \dots + l_n}{n},$$

when n becomes indefinitely great.

If ψ be the velocity before collision of a sphere m' which collides with m, E the angle between the directions of motion



of the two spheres before collision as in the figure, the relative velocity of approach is

$$R = \sqrt{\omega^2 + \psi^2 - 2\omega\psi \cos E}.$$

Let c be the sum of the radii of m and m'. Let $f(\psi)\, d\psi$ be the number of m' spheres in unit of volume. Then the number of collisions which m undergoes with the m' spheres per unit of time is

$$\tfrac{1}{2}\int_0^\infty\int_0^\pi f(\psi)\, d\psi \pi c^2 R \sin E dE = \pi c^2 N_1 \text{ suppose,}$$

and the mean free path for an m moving with velocity ω, if no collisions occur except with spheres of the m' class, is $\lambda_\omega = \dfrac{\omega}{\pi c^2 N_1}$. If there be two classes m_1 and m_2, and m can collide with another sphere of either class, we shall have a corresponding number of collisions per unit of time between m and m_2, which we will denote by $\pi c^2 N_2$. Then the mean free path for velocity ω is $\lambda_\omega = \dfrac{\omega}{\pi c^2 (N_1 + N_2)}$ and so on. To calculate the mean free path is to calculate $N_1 + N_2$, &c.

112. Another method of obtaining this result is as follows.

Let S be the whole space in which our spheres are moving. Consider a sphere m moving with velocity ω, and another sphere m_1 whose velocity and direction of motion are comprised respectively within the limits $\psi \ldots \psi + d\psi$ and $E \ldots E + dE$, as in the figure.

Now m_1 may be anywhere within S. If its centre be at this instant within the cylinder whose base is a circular area of centre m and radius c, the sum of the radii of m and m_1, at right angles to R, and whose height is Rdt, then, but not otherwise, a collision will occur between m and m_1 within the time dt after this instant.

The chance that such collision shall *not* occur is then

$$1 - \frac{\pi c^2 R dt}{S}.$$

Now the number per unit of volume of spheres m_1 whose velocity and direction of motion are comprised within the limits aforesaid is $f(\psi)\, d\psi\, \tfrac{1}{2} \sin E dE$. And therefore the number within S is $Sf(\psi)\, d\psi\, \tfrac{1}{2} \sin E dE$. Let us now assume that the aggregate volume of all the m_1 spheres within S is negligible compared with S. Then the chance that during dt m shall not collide with any one of the class m_1 is

$$\left(1-\frac{\pi c^2 R dt}{S}\right)$$

raised to the power of

$$Sf(\psi)\,d\psi\,\tfrac{1}{2}\sin E dE,$$

that is, in the limit when dt becomes infinitely small,

$$1-\pi c^2 R dt f(\psi)\,d\psi\,\tfrac{1}{2}\sin E dE,$$

and the chance that m shall not during dt collide with any m_1, whatever be the values of ψ or E, is by the same reasoning

$$1-\pi c^2 dt\int_0^\infty\int_0^\pi f(\psi)\,d\psi\,\tfrac{1}{2}R\sin E dE = 1-\pi c^2 dt N_1 \text{ suppose.}$$

Similarly if there be other classes of spheres, m_2, m_3 &c., with which m may collide, the chance that it shall undergo no collision in the time dt is

$$1-\pi c^2 dt\,(N_1+N_2+\&c.) = 1-\pi c^2 dt N,$$

if $N = N_1 + N_2 + \&c.$

By the same reasoning the chance that m shall undergo no collision in n successive intervals of time dt is

$$1-\pi c^2 N n dt = 1-\pi c^2 N t,$$

if $t = ndt$.

Also if λ be the space described in time t

$$\lambda = \omega t, \quad \text{or} \quad t = \frac{\lambda}{\omega}.$$

Therefore the chance that m shall survive for a distance λ without undergoing any collision is $1-\pi c^2 N\dfrac{\lambda}{\omega}$.

Let $$1-\pi c^2 N\frac{\lambda}{\omega} = \phi(\lambda) = \phi.$$

Then ϕ is the proportion of the whole number of spheres m which, starting with velocity ω, traverse the space λ without collision. Also $\phi(\lambda + d\lambda) = \phi(\lambda)\,\phi(d\lambda)$. It follows that

$$\frac{d\phi}{d\lambda} = -\phi\frac{\pi c^2 N}{\omega} = -k\phi, \text{ if } k = \frac{\pi c^2 N}{\omega},$$

and therefore $\phi = C\epsilon^{-k\lambda}$. Also $\phi = 1$ if $\lambda = 0$. Therefore $C = 1$ and $\phi = \epsilon^{-k\lambda}$. Whence if $\bar{\lambda}$ be the mean value of λ given ω

$$\bar{\lambda} = k\int_0^\infty \epsilon^{-k\lambda}\lambda d\lambda = \frac{1}{k} = \frac{\omega}{\pi c^2 N} = \frac{\omega}{\pi c^2 (N_1 + N_2 + \ldots)}$$

which is the same result as we obtained above (111).

The expression

$$\pi c^2 \int_0^\infty d\psi \int_0^\pi \sin E dE f(\psi)\, d\psi \sqrt{\omega^2 + \psi^2 - 2\omega\psi \cos E}$$

can be calculated numerically in terms of πc^2 and h if

$$f\psi = \epsilon^{-hm_1\psi^2}.$$

The fundamental equation.

113. Let G be any quality, *e.g.* mass, colour, charge of electricity, momentum in given direction, &c. which a molecule may possess in greater or less degree, and which it can carry with it unchanged by its own free motion, and which, as regards the aggregate possessed by two colliding molecules is not changed by collision. Suppose a quantity of gas contained in a vertical cylinder of which the height is very small compared with the diameter of the base. Every molecule that enters the cylinder through its upper flat surface shall enter charged with the quantity G_1 on average of our supposed quality G. Every molecule that enters the cylinder through the base shall enter charged on average with the quantity G_0. When the motion has become stationary, every molecule within the cylinder at a height z above the base will be on average charged with a quantity of the thing in question between G_0 and G_1. Let it be called $G(z)$. $G(z)$ in stationary motion will be a function of z.

114. Now consider a layer P_1 of molecules in the cylinder between the planes z_1 and $z_1 + dz_1$. If the molecules within that layer were enclosed between two elastic planes z_1 and $z_1 + dz_1$ for a finite time, the distribution of velocities among the molecules within it would become, under the circumstances supposed, completely independent of the quantity of G which they happened to carry. It would become in the strictest sense of the term "molecular ungeordnet." In other words condition A would prevail.

Collisions would occur within that layer, and any molecule emerging from such collision would be as likely to be moving in any one direction as in any other. The chance of its having any particular direction would be independent of its charge G.

Consequently if any such molecule, having undergone collision within the layer P_1 arrives without further collision at the layer P, the mean quantity of G which it brings with it is the mean quantity of G per molecule for all the molecules within the layer at P_1. This is the fundamental assumption.

115. Now let Gz be the mean value of that quantity for all the molecules within the layer $z \ldots z + dz$ at P. Suppose a molecule to arrive at that layer from above with velocity between v and $v + dv$, and in direction making angle between θ and $\theta + d\theta$ with the vertical. Let λ be the distance which on its arrival at P it has traversed since its last collision. Then such last collision must have occurred at a height $\lambda \cos \theta$ above P. Therefore the quantity of G with which the molecule is charged is the mean quantity of G for the height $z + \lambda \cos \theta$, that is

$$G(z + \lambda \cos \theta) = Gz + \lambda \cos \theta \frac{dG}{dz},$$

because $\lambda \cos \theta$ is small.

The number of molecules which, having velocity and direction between those limits, pass through the horizontal plane P per unit of area and time is $vf(v) \tfrac{1}{2} \sin \theta \cos \theta d\theta dv$.

Hence the quantity of G carried through the layer P per unit of area and time by molecules coming from above is

$$vf(v)\, dv \tfrac{1}{2} \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta G(z)\, d\theta + \tfrac{1}{2} \int_0^{\frac{\pi}{2}} \lambda \cos^2 \theta \sin \theta d\theta \frac{dG}{dz} f(v)\, vdv$$

$$= \left(\tfrac{1}{4} G(z) + \tfrac{1}{6} \lambda \frac{dG}{dz}\right) f(v)\, vdv,$$

and taking the mean of all values of λ and v it is

$$\tfrac{1}{4}G(z) + \tfrac{1}{6}\bar{\lambda}\frac{dG}{dz}.$$

Here $$\bar{\lambda} = \int_0^\infty f(v)\, v\lambda dv.$$

By the same reasoning the quantity of G carried through the layer P per unit of area and time by molecules coming from below is $\tfrac{1}{4}G(z) - \tfrac{1}{6}\bar{\lambda}\frac{dG}{dz}$.

And the quantity passing through P downwards exceeds the quantity passing through P upwards per unit of area and time by $\tfrac{1}{3}\bar{\lambda}\frac{dG}{dz}$.

116. This is the fundamental equation from which Boltzmann calculates the rate of diffusion, viscosity &c. in gases assuming condition A to prevail. It would represent with complete accuracy the initial motion of the system, if the quality G were suddenly attributed to the molecules in the degree proper to z, but without regard to their velocities.

It takes no account, as he points out, of any variation in the distribution of velocities which may be caused by the quality G itself, for if for instance G be momentum in given direction at right angles to the axis of our cylinder, such a change in distribution must exist. It is assumed that the effect of this change in distribution on the mean free path λ is so small as to be negligible, a condition which must be secured if the given terminal conditions, *e.g.* G_0 and G_1, do not differ very widely per unit of distance.

117. The method also takes no account of the stream. The effect is to set up a stream, so to speak, of G from the upper to the lower parts of the cylinder. And that, as will be found, causes a small error in the result. The error may indeed be negligible so long as the stream velocity is very small compared with molecular velocities, which will be the case if the terminal conditions do not differ widely per unit of distance.

It therefore does not sensibly affect the results calculated from Boltzmann's formula in any case to which as I understand he proposes to apply that formula. It is worth while however to consider the sign and order of magnitude of this deviation from complete accuracy.

We are asked to suppose that in stationary motion molecules carrying positive G, have a mean velocity u downwards; molecules carrying negative G have a mean velocity u', u and u' being functions of z. Hydrodynamical considerations make Gu and Gu' sensibly constant throughout the cylinder in stationary motion.

But when collisions take place in the layer P_1, *condition A* is supposed to prevail so that the molecules issuing from collision are as likely to be moving in any one direction as in any other, and to carry with them, in whatever direction they do move, the quantity of G due to the height z.

In fact molecules with positive G, having before collision the mean velocity u downwards, will issue from collision with some mean velocity downwards, less indeed than u but comparable with it, and therefore will not be moving in all directions indifferently, but on the average downwards. And molecules moving downwards will possess on average a greater quantity of G than that due to the layer in which their last collision took place. For let ω be the absolute velocity of a molecule m before collision. Let ψ be the velocity before collision of the other molecule m' concerned, E the angle between their directions as in the figure (Art. 111). Then the velocity of m after collision is the resultant of (1) the common velocity of m and m', (2) their relative velocity, in whatever direction it be, after collision. But for the relative velocity after collision all directions are equally probable. The relative velocity therefore contributes on average nothing to the resultant.

The resultant velocity after collision is then on average the common velocity. And the velocity after collision resolved in its direction before collision is the common velocity resolved in direction ω, that is if $m = m'$ $\omega + \psi \cos E$. We have then for the mean value of the velocity after collision resolved in the direction before collision the expression

$$A\int_0^\infty d\psi\,\epsilon^{-h\psi^2}\,\psi^2\int_0^\pi \sqrt{\omega^2+\psi^2-2\omega\psi\cos E}\,(\omega+\psi\cos E)\sin E\,dE.$$

That can be calculated as a function of ω. As however we intend to treat it as negligible, it is not worth while to calculate it here. But we can easily prove that it is necessarily positive. We may therefore conclude that the mean velocity after collision of a molecule carrying positive G resolved in its direction before collision is $f\omega$ on average, where f is some positive quantity less than unity.

It follows that the mean velocity downwards of the molecules carrying positive G, which before collision was u, is after collision fu.

We have thus proved that the molecules carrying positive G issue from collision in the layer P_1 with mean velocity fu down the cylinder. For the same reason the molecules carrying negative G issue from collision with mean velocity fu_0 upwards. Therefore of the molecules which reach the layer P, having had their last collision in the layer P_1, the proportion which carry positive G is not the same as the proportion of all the molecules within the layer P_1 which carry positive G, as it was assumed to be in forming the fundamental equation, but is greater.

118. *The effect of the introduction of the b coefficients in this case.*

It has been shown in Chapters IV.—VI. that molecules near to one another are on average moving in the same direction. The energy of their relative motion is therefore less than it would be were condition A assumed, and therefore their encounters *pro tanto* less frequent. That tends to increase the mean free path.

On the other hand under assumption B the molecules tend to become aggregated into denser and rarer masses. That tends to increase the frequency of their encounters and therefore to diminish the mean free path.

It is probable that for ordinary gases under ordinary conditions the b coefficients will be very small. And if so the effect of the b coefficients on the phenomena of diffusion &c. will be of the same order of magnitude as those sources of error mentioned in Arts. 116, 117, which as we have said Boltzmann and others have agreed to neglect in calculations concerning these phenomena. I shall not therefore here further consider the effect of the use of assumption B instead of A on such calculations.

CHAPTER X.

ON THE HYPOTHESIS THAT HEAT OR TEMPERATURE IS REPRESENTED BY THE KINETIC ENERGY OF MOLECULAR MOTION.

Natanson's Theorem.

119. M. Ladislas Natanson (Interprétation cinétique de la fonction de dissipation—*Bulletin de l'Académie des Sciences de Cracovie*, Décembre 1893) considers a medium composed of molecules in motion. The components of the molecular velocity of a molecule are u, v, w, those of the apparent or stream velocity of an element of volume are ξ, η, ζ. I have here interchanged Natanson's symbols to make them agree as far as possible with my own, and so avoid confusion. Evidently, taking mean values,

$$\bar{u} = \bar{v} = \bar{w} = 0.$$

Let
$$K = \tfrac{1}{2} \iiint \rho\, (\xi^2 + \eta^2 + \zeta^2)\, dxdydz,$$

ρ denoting density, and

$$E = \tfrac{1}{2} \iiint \rho\, (u^2 + v^2 + w^2)\, dxdydz.$$

The integrations are throughout all space occupied by the system.

120. M. Natanson gives no definition of ξ, η, ζ, but is, as I understand, willing to accept Boltzmann's definition—that ξ at P is the momentum in x of the centre of inertia of all the molecules contained in a sphere of radius r described about P as centre divided by the volume of that sphere, in the limit when r becomes infinitely small.

I should propose myself to define it as in Art. 61 by the function f, so that ξ, η, ζ, Natanson's components of stream velocity, agree nearly with the ξ, η, ζ, of Chapter v. But M. Natanson does not on his own assumption require any further definition.

The normal pressures per unit of surface are

$$p_{xx} = \rho \overline{u}^2, \quad p_{yy} = \rho \overline{v}^2, \quad p_{zz} = \rho \overline{w}^2.$$

The tangential pressures are

$$p_{xy} = \rho \overline{uv}, \quad p_{xz} = \rho \overline{uw}, \quad p_{yz} = \rho \overline{vw}.$$

121. He then gives the following fundamental equation, viz. q being any function of $u + \xi$, $v + \eta$, $w + \zeta$, the time variation of q is found from

$$\rho \frac{dq}{dt} + \frac{d}{dx}(\rho \overline{uq}) + \frac{d}{dy}(\rho \overline{vq}) + \frac{d}{dz} \rho \overline{wq}$$

$$= \rho \frac{\partial q}{\partial t} + X \frac{dq}{d\xi} + Y \frac{dq}{d\eta} + Z \frac{dq}{d\zeta}.$$

Here X, Y, Z are the components of external force, and $\frac{\partial q}{\partial t}$ the change of q due to encounters, $\frac{dq}{dt}$ the total change of q with the time.

Writing $u + \xi$ for q, he finds

$$\rho \frac{d\xi}{dt} + \frac{d}{dx}(\rho \overline{u^2}) + \frac{d}{dy}(\rho \overline{uv}) + \frac{d}{dz}(\rho \overline{uw}) = \rho X, \text{\&c.} \ldots\ldots (4).$$

And again, putting $q = (u + \xi)^2 + (v + \eta)^2 + (w + \zeta)^2$, he obtains, neglecting terms of the third order,

$$\rho \frac{d}{dt}(\xi^2 + \eta^2 + \zeta^2 + \overline{u^2} + \overline{v^2} + \overline{w^2})$$

$$+ \frac{d}{dx}(2\xi\rho\overline{u^2} + 2\eta\rho\overline{uv} + 2\zeta\rho\overline{uw})$$

$$+ \frac{d}{dy}(2\xi\rho\overline{uv} + 2\eta\rho\overline{v^2} + 2\zeta\rho\overline{vw})$$

$$+ \frac{d}{dz}(2\xi\rho\overline{uw} + 2\eta\rho\overline{vw} + 2\zeta\rho\overline{w^2})$$

$$= 2\rho(\xi X + \eta Y + \zeta Z)$$

$$+ \rho \frac{\partial}{\partial t}(\xi^2 + \eta^2 + \zeta^2 + u^2 + v^2 + w^2) \ldots\ldots\ldots\ldots (5).$$

Combining (4) and (5) we get

$$\tfrac{1}{2}\rho\frac{d}{dt}(\overline{u^2}+\overline{v^2}+\overline{w^2})+\rho\overline{u^2}\frac{d\xi}{dx}+\rho\overline{v^2}\frac{d\eta}{dy}+\rho\overline{w^2}\frac{d\zeta}{dz}$$

$$+\rho\overline{vw}\left(\frac{d\eta}{dz}+\frac{d\zeta}{dy}\right)+\rho\overline{uw}\left(\frac{d\zeta}{dx}+\frac{d\xi}{dz}\right)+\rho\overline{uv}\left(\frac{d\xi}{dy}+\frac{d\eta}{dx}\right)$$

$$=\rho\frac{\partial}{\partial t}(\xi^2+\eta^2+\zeta^2+\overline{u^2}+\overline{v^2}+\overline{w^2})\quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6).$$

Let $$\frac{d\xi}{dx}=a,\quad\frac{d\eta}{dy}=b,\quad\frac{d\zeta}{dz}=c,$$

$$\frac{d\eta}{dz}+\frac{d\zeta}{dy}=A,\quad\frac{d\zeta}{dx}+\frac{d\xi}{dz}=B,\quad\frac{d\xi}{dy}+\frac{d\eta}{dx}=C.$$

Add to the first member of (6)

$$\tfrac{1}{2}(\overline{u^2}+\overline{v^2}+\overline{w^2})\frac{d\rho}{dt}+\tfrac{1}{2}\rho(\overline{u^2}+\overline{v^2}+\overline{w^2})(a+b+c),$$

which is zero. Also write

$$\frac{d}{dt}\tfrac{1}{2}\rho(\overline{u^2}+\overline{v^2}+\overline{w^2})$$

$$=\frac{\partial}{\partial t}\tfrac{1}{2}\rho(\overline{u^2}+\overline{v^2}+\overline{w^2})+\left(\xi\frac{d}{dx}+\eta\frac{d}{dy}+\zeta\frac{d}{dz}\right)\tfrac{1}{2}\rho(\overline{u^2}+\overline{v^2}+\overline{w^2}).$$

And then in the equation so obtained integrate for x, y, z, and make $l\xi+m\eta+n\zeta=0$ at the bounding surface, l, m, n being direction cosines of the normal to that surface. Assume further that $X=Y=Z=0$, or no external forces act.

The result is

$$\frac{dE}{dt}+\iiint(\rho\overline{u^2}a+\rho\overline{v^2}b+\rho\overline{w^2}c+\rho\overline{vw}A+\rho\overline{uw}B+\rho\overline{uv}C)\,dxdydz=0.$$

Treating equation (5) in the same way, we obtain

$$\frac{dK}{dt}-\iiint(\rho\overline{u^2}a+\rho\overline{v^2}b+\rho\overline{w^2}c+\rho\overline{vw}A+\rho\overline{uw}B+\rho\overline{uv}C)\,dxdydz=0.$$

And therefore, there being no external forces, $\dfrac{dK}{dt}=-\dfrac{dE}{dt}$, or the kinetic energy of stream motion can increase or diminish only at the expense of molecular energy.

122. Let us now write

$$3p = \rho\overline{u^2} + \rho\overline{v^2} + \rho\overline{w^2},$$

$$F = (p - \rho\overline{u^2})\, a + (p - \rho\overline{v^2})\, b + (p - \rho\overline{w^2})\, c$$
$$- \rho\overline{vw}A - \rho\overline{uw}B - \rho\overline{uv}C.$$

By a further use of the fundamental equation, putting $q = \overline{(u+\xi)^2}$, and then $q = \overline{v+\eta} \times \overline{w+\zeta}$, we find

$$F = -\frac{1}{4p}\frac{\partial}{\partial t}\{(p - \rho\overline{u^2})^2 + (p - \rho\overline{v^2})^2 + (p - \rho\overline{w^2})^2$$
$$+ 2\,(\rho\overline{vw})^2 + 2\,(\rho\overline{uw})^2 + 2\,(\rho\overline{uv})^2\}.$$

And finally

$$\frac{dE}{dt} = -\frac{dK}{dt} = \iiint (F - p\theta)\, dxdydz,$$

where $$\theta = a + b + c = \frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz}.$$

123. It appears then that E, the molecular or heat energy, gains or loses at the expense of the energy of stream motion, according to the law of encounters "loi des chocs moléculaires." If, that is, as the result of encounters the tangential pressures are increasing, E diminishes, and K increases. Now this is precisely what happens according to Chap. V. *ante*, when, for instance, instead of being material points, the molecules become elastic spheres of finite diameter. As the result of collisions in that case ξ^2 in my notation becomes $\xi^2 + \xi'^2$, &c. And as we have seen, Art. 105, $(\overline{\alpha\gamma})^2$, $(\overline{\alpha\beta})^2$, and $(\overline{\beta\gamma})^2$ increase, but only up to a certain point, at which namely the ratio ξ'^2/ξ^2 has the proper value for stationary motion. The relation between the energy of visible motion K and that of molecular motion E is in Natanson's theorem the same as that between K and heat in Thermodynamics.

Messrs Bryan and Boltzmann's method.

124. In order to confirm the hypothesis that the temperature of a gas or other substance is proportional to the mean kinetic energy of its molecules, Messrs Bryan and Boltzmann (*Vienna Sitzungsberichte math. naturw. Classe,* Band III., Abtheil II. Dec. 1894, also referred to by Boltzmann, *Gastheorie,* p. 136, *et seq.*) treat the following case. X and Y are two infinite parallel planes. In the space S_1 to the left of X is a gas A. In the space S_2 to the right of Y another gas B. In the space S between X and Y there acts on molecules of gas A a force directed from Y whose potential becomes infinite on Y, and there acts on molecules of gas B a force directed from X whose potential becomes infinite on X. These conditions insure that no molecule of gas A will be found in S_2, and no molecule of gas B will be found in S_1. But in the space S there will be a mixture of A and B, and encounters will take place between their respective molecules.

Messrs Bryan and Boltzmann use generalised coordinates, but it will be sufficient in this notice to deal only with velocities of translation, as though both A and B molecules were elastic spheres.

It is assumed that the mean kinetic energy of A molecules at any point within S is the same as their mean kinetic energy within S_1, and that the mean kinetic energy of B molecules within S is the same as their mean kinetic energy within S_2.

It is assumed further that as the result of encounters taking place within S, between A and B, the molecules of A acquire, if they have it not already, the same mean kinetic energy as those of B. That result seems to me to be questionable or to be only approximately true, if the molecules have finite diameters or spheres of action. But I state this with diffidence when such authorities are against me.

Making however these two assumptions, the conclusion follows that the mean kinetic energy for the A molecules in S_1 must become equal to that of the B molecules in S_2. And therefore that if the mean kinetic energy be originally different for A and for B, a finite quantity of energy will pass from S_1 to S_2, or *vice versa*.

The condition that no energy shall pass is that the mean kinetic energy shall be the same for A as for B. But we may regard the two gases as two bodies in contact, which condition is more nearly realised as S is diminished indefinitely. The known experimental condition that no energy shall pass between two bodies in contact is that both shall be at the same temperature. Hence in the case of the two gases at all events kinetic energy plays the same part as temperature.

Professor J. J. Thomson's method.

125. The same hypothesis is tested in a different way by Professor J. J. Thomson (*Application of Dynamics to Physics and Chemistry*, p. 91). He puts the following case. Suppose a tube in which is moveable a piston of very great mass M. On one side of it is a set A of material particles each of mass m_1 in motion. On the other side a set B of material particles each of mass m_2 in motion. Considering the two systems of particles as two substances, and the piston as a conductor of heat, the condition that no heat shall pass through the piston from one substance to the other is that the two substances shall be at the same temperature. If temperature be represented by kinetic energy of translation, then the condition that neither set of particles shall on average either lose or gain energy by collisions with the piston ought to be that the mean kinetic energy of translation is the same for the A as for the B set.

Let U be the velocity of the piston, u_1 the velocity normal to the surface of the piston of a particle m_1 before impact. It is assumed that particles striking the piston rebound from it as perfectly elastic bodies. Let U', u_1' denote the values which U, u_1 assume after impact. Then we have

$$m_1u_1 + MU = m_1u_1' + MU',$$

$$m_1u_1^2 + MU^2 = m_1u_1'^2 + MU'^2.$$

From which deduce

$$m_1(u_1'^2 - u_1^2) = \frac{4M^2m_1U^2 - 4Mm_1(M - m_1)Uu_1 - 4Mm_1^2u_1^2}{(M + m_1)^2} \quad (a).$$

Now add together the equations of this form for all collisions which take place in unit of time. Let N_1 be the number of such collisions. Also let $\theta = \frac{1}{2}MU^2$ be the kinetic energy of the piston, and θ_1 the mean kinetic energy of the particles of the set A which strike the piston. As I understand Professor Thomson, the mean is taken for all collisions, not for all particles.

It is assumed that the velocity U of the piston is zero on average of time, because the piston is being struck on the other side by particles of the B set and the pressure is supposed to be the same on either side. Hence we may neglect in the expression (a) the term which contains U in the first degree.

The expression then takes the form

$$N_1\partial\theta_1 = N_1(2\theta - \tfrac{1}{3}\theta_1)\frac{2Mm_1}{(M+m_1)^2} \quad \ldots\ldots\ldots\ldots\ldots(1).$$

NOTE. This should, I think, be $\frac{2}{3}\theta_1$ instead of $\frac{1}{3}\theta_1$ because as $MU^2 = 2\theta_1$ so $m_1u_1^2 = \frac{2}{3}\theta_1$, θ_1 denoting the whole mean kinetic energy of all molecules which collide with the piston or with other portions of the elastic surface bounding the A molecules, *i.e.*

$$2\theta_1 = m_1(\overline{u_1^2} + \overline{v_1^2} + \overline{w_1^2}).$$

But this does not affect Professor Thomson's argument.

Similarly for the B set we have

$$N_2\partial\theta_2 = N_2(2\theta - \tfrac{1}{3}\theta_2)\frac{2Mm_2}{(M+m_2)^2} \ldots\ldots\ldots\ldots\ldots(2),$$

and since $\partial\theta = -N_1\partial\theta_1 - N_2\partial\theta_2 = 0$ on average

$$N_1\frac{2Mm_1}{(M+m_1)^2}(2\theta - \tfrac{1}{3}\theta_1) + N_2\frac{2Mm_2}{(M+m_2)^2}(2\theta - \tfrac{1}{3}\theta_2) = 0.$$

If $$a = \frac{N_2m_2}{(M+m_2)^2}, \quad b = \frac{N_1m_1}{(M+m_1)^2}.$$

This gives $$2\theta - \tfrac{1}{3}\theta_1 = \frac{a}{a+b}\tfrac{1}{3}(\theta_2 - \theta_1),$$

$$2\theta - \tfrac{1}{3}\theta_2 = \frac{b}{a+b}\tfrac{1}{3}(\theta_1 - \theta_2).$$

Substituting in (1) and (2)

$$\partial\theta_1 = \frac{2Mab}{3(a+b)}(\theta_2 - \theta_1),$$

$$\partial\theta_2 = -\frac{2Mab}{3(a+b)}(\theta_2 - \theta_1),$$

and therefore $\partial\theta_1 = \partial\theta_2 = 0$, if $\theta_1 = \theta_2$.

It follows that if $\theta_2 > \theta_1$ the effect of all the collisions is to increase θ_1 at the expense of θ_2, and *vice versa*. And the condition that no energy shall pass from A to B or from B to A is that $\theta_2 = \theta_1$, or the mean kinetic energy of translation for *all particles colliding with the piston* is the same for A as for B.

126. Now let $f(u)\,du$ be the number per unit of volume of particles of the A set whose velocities normal to the piston lie between u and $u + du$. Then the number of such particles which strike the piston per unit of area and time is $\int_0^\infty f(u)\,u\,du$. The sum of the kinetic energies of their motion normal to the piston is $\frac{1}{2}m_1\int_0^\infty f(u)\,u^3 du$. The mean kinetic energy of motion normal to the piston for all A particles irrespective of their striking the piston is $\frac{1}{2}m_1\int_0^\infty f(u)\,u^2 du$. Let $f(u)$ be so chosen that the ratio

$$\frac{\int_0^\infty f(u)\,u^3\,du}{\int_0^\infty f(u)\,u\,du} : \frac{\int_0^\infty f(u)\,u^2\,du}{\int_0^\infty f(u)\,du},$$

is an absolute constant, and therefore the same for A as for B. That being the case, when $\theta_1 = \theta_2$, or the mean kinetic energy per collision is the same for A as for B, the mean kinetic energy per particle is also the same for A as for B. And therefore the condition that on the whole there shall be no transfer of energy through the piston from A to B or *vice versa* is that the mean kinetic energy per particle is the same for A as for B.

127. If we assume for A particles

$$f(u_1) = C_1 \epsilon^{-hm_1u_1^2},$$

and for B particles $f(u_2) = C_2 \epsilon^{-hm_2u_2^2}$,

we satisfy the condition.

Possibly there may be other forms of $f(u)$ which satisfy it. But however this may be, some assumption with regard to the relative frequency of different values of u appears to be necessary.

Further, $f(u)$ being properly chosen, we satisfy at the same time the two conditions (1) that the pressure shall be the same on either side of the piston, the number of particles per unit of volume being the same for A as for B, and (2) that there shall be no transfer of energy.

The law of distribution of velocities thus appears to be of the essence of the matter, if the molecular motion is to represent heat.

The Second Law of Thermodynamics.

128. Our gas system being in stationary motion according to the laws above investigated, we might impart to it a certain quantity of heat δE. That being done, it would assume a new form of stationary motion, in which the mean kinetic energy T, the volume ω, and the mean potential energy χ, will be generally different from what they were in the original motion. If P be the external pressure which in the original motion was just sufficient to prevent expansion, the change of volume $\partial\omega$ can be effected only by doing an amount of work $P\partial\omega$ against the external force P. A part of the energy ∂E supplied to the system is spent in doing this work. The remainder is spent in increasing either (1) the mean kinetic energy T, or (2) the mean potential energy, $\bar{\chi}$, of the intermolecular forces, so that $\partial E = \lambda\partial T + \partial\bar{\chi} + P\partial\omega$, λ being the number of molecules.

129. If the external forces P also have a potential, there is in general a determinate relation between $\partial\omega$ and ∂T, and a determinate relation between $\partial\omega$ and $\partial\chi$. So that in this case there is only one independent variable, and no question can arise whether or not $\frac{\partial E}{T}$ is a complete differential. Any theorem proved on the hypothesis of P having a potential is not the Second law of Thermodynamics as usually understood.

But the external force P is in Professor Thomson's language a "controllable" force. It is possible therefore by suitably varying P to maintain the system in stationary motion with any arbitrarily assigned values of T and ω. But ∂T and $\partial \omega$ being given, $\partial \chi$ is determinate. There are then, P being controllable, two independent variables. It is convenient to use P and ω for independent variables.

130. If in rectangular coordinates the abscissa represents ω, and the ordinate represents P, any point in the diagram represents a determinate state of the system, in which it is in stationary motion with the values of P and ω corresponding to the point, it being understood that the controllable force P is to have such value given to it as will be necessary to maintain that motion stationary. So also any curve drawn on the plane of the diagram represents a series of states through which the system might be made to pass successively, P being made to vary as required. But it is understood that the change of state, that is the passage from one point in the curve to another, is effected so slowly that stationary motion is always attained, and therefore the kinetic energy corresponding to the controllable coordinate ω is for our purpose to be taken as zero.

If the curve be a closed curve, the system having passed through all the states denoted by the curve, has at the end of the process the same values of P and ω, and is therefore for all experimental purposes in the same condition as it was at the beginning. Contemplating the system itself alone, nothing that we can observe by experiment has happened to it. Now if θ denote the absolute temperature, the second law of Thermodynamics asserts that in this complete cycle $\int \frac{\partial E}{\theta} = 0$, or $\frac{\partial E}{\theta}$ is a complete differential of some function of θ and ω.

That function was called by some writers the *Thermodynamic function*, by others the *Entropy* of the system.

131. As I have said, $\frac{\partial E}{\theta}$ being a complete differential, no change takes place in the system itself as the result of any complete cycle of operations of the kind described. But $\int \partial E \neq 0$, and $\int P \partial \omega \neq 0$. Generally a quantity of heat denoted by $\int \partial E$, drawn from some external source, has been converted into mechanical work $\int P \partial \omega$ outside of the system, and a further quantity has been transferred from a hotter to a colder external body, as shown in treatises on Thermodynamics. But if our system be enclosed in a non-conducting envelope, so that no heat or other form of energy is allowed to pass into it from without, or out of it into external space, it may by suitably varying the controllable P be made to expand or be compressed, and in so doing it does external work, positive in case of expansion, negative in case of compression. This work is done at the expense either of the absolute temperature θ or of the potential χ of the system itself. The line traced on the diagram in such a process, a line that is for which $\partial E = 0$, is called an adiabatic line. If the cycle be $ABCD$ on the diagram, AB denoting expansion at constant absolute temperature θ, BC adiabatic, CD compression at constant absolute temperature θ', and DA adiabatic, it is found that the heat which must be supplied from without to effect the expansion AB is to the heat withdrawn during the compression CD, both measured in mechanical units, as $\theta : \theta'$. If temperature is represented by the kinetic energy, we ought to find $T : T' :: \theta : \theta'$, or $\frac{\partial E}{T}$ is a complete differential.

132. In the *Philosophical Magazine*, January, 1876, a proof of this proposition was given by the present writer. This was employed afterwards in an improved form by Dr Watson in his *Kinetic Theory of Gases*, and has been accepted by Professor Bryan. It was founded, as will be seen, on Boltzmann's theorem, that the chance of a group of λ molecules having their coordinates between the limits

$$x_1 \ldots x_1 + dx_1,$$
$$\ldots\ldots\ldots\ldots\ldots$$
$$z_\lambda \ldots z_\lambda + dz_\lambda,$$

(in which position their potential is χ) is proportional to

$$\epsilon^{-h\chi}\, dx_1 dy_1 \ldots dz_\lambda .$$

This is established only on the assumption of condition A. I will here give that proof of the second law in order that we may subsequently see what modifications are required in it when we abandon condition A, and employ the more general method of this work. I here use h instead of $2h$ of Art. 44.

We have $$\partial E = \lambda \partial T + \partial \bar{\chi} + P \partial \omega .$$

Let $T = \frac{3}{2h}$ = the mean kinetic energy of a molecule.

Then $$\frac{1}{T} = \frac{2h}{3},$$

and $$\frac{\partial E}{T} = \lambda \frac{2h}{3} \partial T + \frac{2h}{3} \partial \bar{\chi} + \frac{2h}{3} P \partial \omega \ldots\ldots\ldots\ldots\ldots (\text{I}).$$

Now substitute for $P\partial\omega$ from Clausius' equation, Art. 24,

$$\tfrac{3}{2} P \omega = \Sigma \tfrac{1}{2} m (u^2 + v^2 + w^2) + \tfrac{1}{2} \Sigma \Sigma \overline{Rr},$$

or $$P \partial \omega = \tfrac{1}{3} \Sigma m (u^2 + v^2 + w^2) \frac{\partial \omega}{\omega} + \tfrac{1}{3} \Sigma \Sigma \overline{Rr} \frac{\partial \omega}{\omega} .$$

Now if there be a general cubical expansion, ω becoming $\omega + \partial \omega$, every line r in the system becomes

$$r + \tfrac{1}{3} \frac{\partial \omega}{\omega} r,$$

or $$\partial r = \tfrac{1}{3} \frac{\partial \omega}{\omega} r.$$

Therefore the last equation becomes

$$P \partial \omega = \tfrac{1}{3} \Sigma m (u^2 + v^2 + w^2) \frac{\partial \omega}{\omega} + \Sigma \Sigma \overline{R \partial r}.$$

Again, for each configuration

$$\Sigma\Sigma R\partial r = -\partial\chi = -\frac{d\chi}{d\omega}\partial\omega.$$

Hence taking mean values

$$\Sigma\Sigma \overline{R\partial r} = -\overline{\frac{d\chi}{d\omega}}\,\partial\omega.$$

Here $\overline{\frac{d\chi}{d\omega}}$ is the mean for all configurations of $\frac{d\chi}{d\omega}$, that is the mean of a variation, while $\partial\overline{\chi}$ is the variation of a mean. The distinction between $\partial\overline{\chi}$ and $\overline{\frac{d\chi}{d\omega}}\partial\omega$ is of the essence of the matter.

Again,

$$\tfrac{2}{3}\Sigma m\,(\overline{u^2} + \overline{v^2} + \overline{w^2})\frac{\partial\omega}{\omega} = \frac{\lambda}{h}\frac{\partial\omega}{\omega},$$

if λ be the number of molecules of the system.

We have then

$$P\partial\omega = \frac{\lambda}{h}\frac{\partial\omega}{\omega} - \overline{\frac{d\chi}{d\omega}}\,\partial\omega,$$

and
$$\frac{2h}{3}P\partial\omega = \tfrac{2}{3}\lambda\frac{\partial\omega}{\omega} - \frac{2h}{3}\overline{\frac{d\chi}{d\omega}}\,\partial\omega.$$

And therefore

$$\frac{\partial E}{T} = \lambda\frac{2h}{3}\partial T + \frac{2h}{3}\partial\overline{\chi} + \tfrac{2}{3}\lambda\frac{\partial\omega}{\omega} - \frac{2h}{3}\overline{\frac{d\chi}{d\omega}}\,\partial\omega \;\ldots\ldots\text{(II)}.$$

133. So far our equation is derived from physical considerations.

Now consider the auxiliary function

$$u = \log\iiint_{-\infty}^{+\infty} e^{-h\chi}\,dx_1\ldots dz_\lambda.$$

Then
$$\partial u = \frac{du}{dh}\partial h + \frac{du}{d\omega}\partial\omega,$$

and
$$\frac{du}{dh}\partial h = \frac{1}{\iiint e^{-h\chi}\,dx_1\ldots dz_\lambda}\,\partial\iiint e^{-h\chi}\chi dx_1\ldots dz_\lambda$$

$$= -\overline{\chi}\partial h,$$

because, since the chance of the configuration $x_1 \ldots z_\lambda$ is

$$\epsilon^{-h\chi}\, dx_1 \ldots dz_\lambda,$$

evidently

$$\bar{\chi} = \iiint - \epsilon^{-h\chi}\, \chi dx_1 \ldots dz_\lambda \div \iiint \epsilon^{-h\chi}\, dx_1 \ldots dz_\lambda .$$

Again, $$\frac{d\bar{u}}{d\omega}\partial\omega = - \frac{1}{\iiint \epsilon^{-h\chi}\, dx_1 \ldots dz_\lambda} \iiint \epsilon^{-h\chi}\, h \frac{d\chi}{d\omega}\, dx_1 \ldots dz_\lambda$$

$$+ \frac{1}{\iiint \epsilon^{-h\chi}\, dx_1 \ldots dz_\lambda} \iiint \epsilon^{-h\chi}\, \partial\,(dx_1 \ldots dz_\lambda),$$

the last term being necessary because every element of length $dx_1 \ldots$ is increased in the ratio $1 : 1 + \frac{1}{3}\frac{\partial\omega}{\omega}$ by the general cubical expansion above mentioned.

That is $$\frac{d\bar{u}}{d\omega}\partial\omega = - h \frac{d\bar{\chi}}{d\omega}\partial\omega + \frac{\lambda}{\omega}\partial\omega,$$

because $$\partial\,(dx_1 \ldots dz_\lambda) = \lambda \frac{\partial\omega}{\omega},$$

and $$\partial\bar{u} = - \bar{\chi}\partial h - h \frac{d\bar{\chi}}{d\omega} + \frac{\lambda\partial\omega}{\omega},$$

or $$\tfrac{2}{3}\lambda \frac{\partial\omega}{\omega} - \tfrac{2}{3}h \frac{d\bar{\chi}}{d\omega}\partial\omega = \tfrac{2}{3}\partial\bar{u} + \tfrac{2}{3}\bar{\chi}\partial h \ldots\ldots\ldots \text{(III)}.$$

Substitute this in (II), and we have

$$\frac{\partial E}{T} = \lambda\partial \log T + \tfrac{2}{3}\,\partial\,(h\bar{\chi}) + \tfrac{2}{3}\partial\bar{u},$$

which is a complete differential.

134. Let us now consider what modification has to be made in the above proof when Q, instead of being the sum of squares of the velocities, has the value given to it in this treatise.

With the form of Q containing the b coefficients, the relative frequency of the several configurations is different from what it was when Q was a sum of squares only, but the values of χ and $\frac{d\chi}{d\omega}$ are not altered for any given configuration. Hence χ and $\frac{\overline{d\chi}}{d\omega}$ have different values from those which they had in the former case, χ and $\frac{d\chi}{d\omega}$ are the same as in the former case. Also $T = \frac{3}{2\mu h} = \frac{3}{2h'}$.

Nevertheless the physical equation

$$\partial E = \lambda \partial T + \partial \chi + P \partial \omega \quad \text{..................(I)}$$

remains unchanged in form with the altered value of χ. Further when we substitute Clausius' expression (Art. 24) for $P\partial\omega$, the equation

$$\frac{\partial E}{T} = \lambda \partial \log T + \frac{2h'}{3} \partial \chi + \tfrac{2}{3}\lambda \frac{\partial \omega}{\omega} - \frac{2h'}{3} \frac{\overline{d\chi}}{d\omega} \partial \omega \quad \text{......(II)}$$

remains unchanged in form with the altered values of h, χ, and $\frac{\overline{d\chi}}{d\omega}$.

Now let us consider the auxiliary function u. We might in the proof above given have put it in the form

$$u = \log \iiint \left(\frac{h}{\pi}\right)^{\frac{\lambda}{2}} \epsilon^{-h\,(\chi + \Sigma(\alpha^2 + \beta^2 + \gamma^2))}\, dx_1 \ldots dz_\lambda d\alpha_1 \ldots d\gamma_\lambda.$$

In our present problem it would then take the form

$$u = \log \iiint \epsilon^{-h'\chi} \left(\frac{h}{\pi}\right)^{\frac{\lambda}{2}} \sqrt{D}\, \epsilon^{-hQ}\, dx_1 \ldots dz_\lambda d\alpha_1 \ldots d\gamma_\lambda$$

$$= \log \iint \epsilon^{-h'\chi} \left(\frac{h}{\pi}\right)^{\frac{\lambda}{2}} \sqrt{D}\, \epsilon^{-hQ} ds\, d\sigma,$$

where ds stands for $dx_1 \ldots dz_\lambda$ and $d\sigma$ for $d\alpha_1 \ldots d\gamma_\lambda$. Then h' and ω are the two independent variables. Let

$$\left(\frac{h}{\pi}\right)^{\frac{\lambda}{2}} \sqrt{D}\, \epsilon^{-hQ} = F.$$

Then $$\partial u = \frac{du}{dh'} \partial h' + \frac{du}{d\omega} \partial \omega.$$

Now $\frac{du}{dh'}\partial h'$

$$= \frac{-\partial h'}{\iint \epsilon^{-h'\chi} F ds d\sigma} \iint \epsilon^{-h'\chi}\left(F\frac{d}{dh'}(h'\chi) - \frac{dF}{dh'}\right) ds d\sigma$$

$$= \frac{-\partial h'}{\iint \epsilon^{-h'\chi} F ds d\sigma} \iint \epsilon^{-h'\chi}\left(F\chi - \frac{dF}{dh'}\right) ds d\sigma$$

$$= -\bar{\chi}\partial h' + \frac{1}{\iint \epsilon^{-h'\chi} F ds d\sigma} \iint \epsilon^{-h'\chi}\partial h' \frac{dF}{dh'} ds d\sigma \text{ ......(1).}$$

Again $\frac{du}{d\omega}\partial\omega$

$$= \frac{-\partial\omega}{\iint \epsilon^{-h'\chi} F ds d\sigma} \iint \epsilon^{-h'\chi}\left(F\frac{d}{d\omega}(h'\chi) - \frac{dF}{d\omega}\right) ds d\sigma,$$

$$+ \frac{\partial\omega}{\iint \epsilon^{-h'\chi} F ds d\sigma} \iint \epsilon^{-h'\chi} F \frac{d}{d\omega}(ds d\sigma),$$

the last term referring to the variations of all the elements of length dx, dy, dz, consequent on the expansion denoted by $\partial\omega$.

That is $\frac{du}{d\omega}\partial\omega$

$$= \frac{-\partial\omega}{\iint \epsilon^{-h'\chi} F ds d\sigma} \iint \epsilon^{-h'\chi}\left(Fh'\frac{d\chi}{d\omega} - \frac{dF}{d\omega}\right) ds d\sigma$$

$$+ \lambda\frac{\partial\omega}{\omega}$$

$$= \lambda\frac{\partial\omega}{\omega} - h'\frac{d\chi}{d\omega}\partial\omega$$

$$+ \frac{\partial\omega}{\iint \epsilon^{-h'\chi} F ds d\sigma} \iint \epsilon^{-h'\chi} \frac{dF}{d\omega} ds d\sigma \text{ ....(2).}$$

Adding together (1) and (2) we find

$$\partial u = -\bar{\chi}\,\partial h' - h'\frac{d\bar{\chi}}{d\omega}\partial\omega + \lambda\frac{\partial\omega}{\omega}$$

$$+\frac{1}{\iint \epsilon^{-h'\chi} F\,ds\,d\sigma}\iint \epsilon^{-h'\chi}\left(\partial h'\frac{dF}{dh'} + \partial\omega\frac{dF}{d\omega}\right)ds\,d\sigma.$$

But now $\iint F\,d\sigma = \frac{3\lambda}{2}$ is constant whatever be the values of h and ω or h' and ω. It is therefore not affected by the variations of h' and ω.

These variations affect neither the quantities $\alpha_1 \dots \gamma_\lambda$, nor the limits of the $d\sigma$ integration.

We have then

$$\frac{\partial E}{T} = \lambda\partial\log T + \tfrac{2}{3}\partial(h'\chi) + \tfrac{2}{3}\partial u,$$

a result of precisely the same form as in the former case.

135. In any case in which

$$\partial\chi = \frac{d\chi}{d\omega}\partial\omega,$$

the proof of the second law for the two independent variables T and ω can be presented in a simple form.

For we have in that case from II

$$\frac{\partial E}{T} = \lambda\partial\log T + \tfrac{2}{3}\lambda\frac{\partial\omega}{\omega}.$$

Now let $i = \frac{\omega^{\frac{1}{3}}}{T^{\frac{1}{2}}}$, that is i is the time in which a particle moving with the velocity of mean square would describe a distance proportional to the linear dimensions of the system.

Then $$\tfrac{2}{3}\partial\log\omega = 2\partial\log i + \partial\log T,$$

and therefore

$$\frac{\partial E}{T} = \lambda\partial\log T + \tfrac{2}{3}\lambda\frac{\partial\omega}{\omega}$$

$$= 2\lambda\partial\log(iT).$$

We might define $\lambda 2iT$ as the *Action of the system* par excellence. With that definition the Action is the same for all states of the system defined by $\partial E = 0$, that is for all states of the system on the same adiabatic line. And we may say that the thermodynamic function ϕ, $\left(\frac{\partial E}{T} = \partial \phi\right)$ either is, or is proportional to, the Action.

136. But $\partial \bar{\chi} = \frac{d\chi}{d\omega} \partial \omega$ cannot exist for any system such as we have treated as a gas, except for a so-called perfect gas in which $\chi = 0$. If there be a potential χ at all, the relative frequency of different configurations of the molecules must generally vary when T varies. And therefore although for any configuration the change of χ as ω varies is independent of T, yet the mean of all values of χ will not be independent of T, because the variation of T causes some configurations, *i.e.* some values, to be represented with greater, and others with less frequency. We may for instance conceive a case in which the molecules placed at equal distances from each other would exert no sensible forces on each other by reason of their distances, and so $\chi = 0$. If we set them in motion they will in some cases approach so near to each other that $\bar{\chi} \neq 0$.

137. Professor J. J. Thomson in the work above referred to gives a proof, not, as he says, of the second law of Thermodynamics, but of a proposition analogous thereto. He does not confine himself to the two variables T and ω, but employs T with any number of controllable coordinates ϕ. Then he assumes that the mean potential energy χ, or in his notation V, is completely fixed by the controllable coordinates, that is, is not a function of T. That restriction prevents Professor Thomson's proof from being applicable to gases, as a proof that $\frac{\partial E}{T}$ is a function of temperature and volume, except in the limiting case of a perfect gas in which V is non-existent. Nor does Professor Thomson propose to apply it to such cases. It may well be that in the more general class of problems treated of in his work the condition that V shall be a function of the controllable coordinates is not a serious restriction.

138. The following is another form of solution of this problem. Let there be, instead of the one controllable coordinate ω, any number of them as $\omega_1 \dots \omega_n$. We will now use ω as a type controllable coordinate. It is assumed that the rate of change of any ω with the time is so slow that we may leave the velocities $\dot{\omega}_1 \dots \dot{\omega}_n$ out of account. Let $V_1 \dots V_n$ be the generalised components of momentum corresponding to $\omega_1 \dots \omega_n$. Then it is a characteristic of the stationary motion that every $\frac{dV}{dt}$ is zero. And therefore if $p_1 \dots p_n$ be the components of external force required to maintain the motion stationary

$$p = \frac{dT}{d\omega} - \frac{d\chi}{d\omega} \text{ for each } \omega,$$

by Lagrange's equations. See Art. 24.

Generally let F be the function denoting frequency, that is F is a function of the coordinates $x_1 \dots z_n$, and the velocities $\alpha_1 \dots \gamma_n$, of the molecules of the system such that the time during which on average of any very long time, they lie between the limits

$$\begin{gathered} x_1 \dots x_1 + dx_1, \\ \dots\dots\dots\dots\dots \\ z_n \dots z_n + dz_n, \\ \alpha_1 \dots \alpha_1 + d\alpha_1, \\ \dots\dots\dots\dots\dots \\ \gamma_n \dots \gamma_n + d\gamma_n, \end{gathered}$$

is $Fdx_1 \dots dz_n d\alpha_1 \dots d\gamma_n$, or as we may write for brevity $Fdsd\sigma$.

Then the mean value of any function as χ is

$$\bar{\chi} = \iint \chi F ds d\sigma \Big/ \iint F ds d\sigma,$$

$$\overline{\frac{d\chi}{d\omega}} = \iint \frac{d\chi}{d\omega} F ds d\sigma \Big/ \iint F ds d\sigma, \text{ \&c.}$$

And $$\partial\bar{\chi} = \iint (\chi \partial F + F \partial \chi)\, ds d\sigma \Big/ \iint F ds d\sigma.$$

In the same case we have, if τ represent the kinetic energy in any particular state, T the mean value of τ,

$$T = \iint \tau F ds d\sigma,$$

$$\partial T = \iint \tau \partial F ds d\sigma + \iint F \partial \tau ds d\sigma$$

$$= \iint \tau \partial F ds d\sigma + \iint F \frac{d\tau}{d\omega} \partial \omega ds d\sigma.$$

139. Let us at this point assume the function F to be a product of two functions, $F = ff'$, where f is a function of the coordinates only. In that case we have also

$$\bar{\chi} = \int \chi f ds \bigg/ \int f ds,$$

$$\partial \chi = \left\{ \int \chi \partial f ds + \int f \frac{d\chi}{d\omega} \partial \omega ds \right\} \bigg/ \int f ds.$$

or

$$\partial \bar{\chi} - \frac{d\chi}{d\omega} \partial \omega = \int \chi \partial f ds \bigg/ \int f ds.$$

And now

$$\partial E = \partial T + \partial \chi + p \partial \omega$$

$$= \partial T + \partial \chi - \frac{d\chi}{d\omega} \partial \omega + \frac{d\tau}{d\omega} \partial \omega$$

$$= 2\partial T + \int \chi \partial f ds - \iint \tau \partial F ds d\sigma,$$

because

$$\frac{d\tau}{d\omega} \partial \omega = \iint F \frac{d\tau}{d\omega} \partial \omega ds d\sigma$$

$$= \partial T - \iint \tau \partial F ds d\sigma,$$

therefore

$$\frac{\partial E}{T} = 2\partial \log T + 2 \int \frac{\chi}{T} \partial f ds - \iint \frac{\tau + \chi}{T} \partial F ds d\sigma.$$

And now we make $\frac{\partial E}{T}$ a complete differential by assuming

$$F = \phi\left(\frac{\tau + \chi}{T}\right), \quad f = \psi\left(\frac{\chi}{T}\right),$$

where ϕ and ψ are any functional symbols.

A solution of these equations is

$$F = Ce^{-h(\chi+\tau)}, \quad f = C'e^{-h\chi},$$

where C, C' are the known constants.

This solution is the one we should take under the assumption of condition A. Another solution is

$$f = C'e^{-h\mu\chi}, \quad F = Ce^{-h\mu(\chi+T)} = Ce^{-h\mu\chi}e^{-hQ},$$

if $Q = \mu T$. This is the solution corresponding to Chap. VIII.

The subject of the Second Law of Thermodynamics has been very fully investigated by Professor G. H. Bryan in his Report on the present state of our knowledge of Thermodynamics, Part II., British Association, 1894

APPENDIX.

MATHEMATICAL PROPOSITIONS.

In the preceding chapters I have assumed without proof certain propositions relating chiefly to determinants. They are for the most part very simple, but as some readers may think they require proof, I will devote this chapter to proving them. I shall require to make use of the following elementary property of determinants. If each of the constituents in one row is equal to the corresponding constituent in a second row multiplied by a constant factor, the determinant is zero. The two rows for which this is the case are said to be *similar*. Whatever general proposition is proved of rows is of course equally true of columns.

(*a*) Let us take for a type determinant of n^2 constituents

$$D = \begin{vmatrix} C_{11}, & C_{12} \ldots C_{1n}, \\ C_{21}, & C_{22} \ldots C_{2n}, \\ \ldots\ldots & \ldots\ldots\ldots \\ C_{n1}, & C_{n2} \ldots C_{nn}, \end{vmatrix}$$

in which C_{pq} is the constituent (whatever its value) in the pth row and qth column, and C_{12} is not necessarily equal to C_{21}, &c. This can be made to represent any given determinant by assigning proper values to the constituents C.

Let D_{pq} denote the minor of D formed by omitting the pth row and qth column, that is by striking out C_{pq} and the row and column in which it is; D_{qp} the minor formed by omitting C_{qp}. In the determinant or any of its minors the diagonal from the first constituent in the top row to the last in the bottom row shall be called the *axis*, and its constituents *axial constituents.*

(*b*) The sign of D_{pq} shall be such that

$$\begin{aligned} D &= C_{11}D_{11} + C_{12}D_{12} + \ldots + C_{1n}D_{1n} \\ &= C_{21}D_{21} + C_{22}D_{22} + \ldots + C_{2n}D_{2n} \\ &= \&c. \end{aligned}$$

In order that this may be the case, we must in forming any minor D_{pq} apply the following rule of signs, namely to the product of all the axial constituents of that minor the positive or negative sign is to be attributed according as $p+q$ is even or odd, and we deduce therefrom the sign of the product of any other set of constituents of the minor according to the usual rule in expanding determinants. In like manner D_{prqs} shall denote the minor formed by omitting C_{pq} and C_{rs} and the rows and columns in which they are. It follows from the above convention concerning signs that

$$nD = \sum_{p=1}^{p=n} \sum_{q=1}^{q=n} C_{pq} D_{pq}.$$

Then evidently $\dfrac{dD}{dC_{pq}} = D_{pq}$, whatever values p and q may have.

(*c*) Now consider the new determinant

$$D' = \left| \begin{array}{l} C_{11} - \theta_1 x_1, \ C_{12} - \theta_1 x_2 \ldots C_{1n} - \theta_1 x_n, \\ C_{21} - \theta_2 x_1, \ C_{22} - \theta_2 x_2 \ldots C_{2n} - \theta_2 x_n, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ C_{n1} - \theta_n x_1, \ C_{n2} - \theta_n x_2 \ldots C_{nn} - \theta_n x_n. \end{array} \right|$$

If all the C's in any two rows, as the pth and qth, were zero, D' would be zero, because the pth and qth rows would then be similar. It follows that every term in D contains at least $n-1$ C factors, and therefore that D' contains no products of any two or more of the new partial constituents θx. For such products necessarily enter in pairs equal and of opposite sign, as for instance $\theta_1 x_2 \theta_2 x_1 - \theta_1 x_1 \theta_2 x_2$.

Therefore $$D' = D - \Sigma\Sigma\theta_p x_q D_{pq}.$$

(*d*) Now form a new determinant of $(n+1)^2$ constituents by adding to D an $(n+1)$th row and $(n+1)$th column. The $(n+1)$th row shall be

$$\beta_{(n+1)1},\ \beta_{(n+1)2}\dots\beta_{(n+1)n},\ 2a_{n+1},$$

and the $(n+1)$th column shall be symmetrical with it, containing $\beta_{1(n+1)}$ in the first row, $\beta_{2(n+1)}$ in the second, and so on. Also let $\beta_{pq}=\beta_{qp}$, for all values of p and q.

Let Δ be that new determinant, namely

$$\Delta = \begin{vmatrix} C_{11},\ C_{12}\dots C_{1n},\ \beta_{1(n+1)}, \\ C_{21},\ C_{22}\dots C_{2n},\ \beta_{2(n+1)}, \\ \dots\dots\dots\dots\dots\dots\dots\dots \end{vmatrix}$$

(*e*) Next in D' write

$$\theta_1 x_1 = \frac{\beta_{1(n+1)}^2}{2a_{n+1}},\quad \theta_1 x_2 = \frac{\beta_{1(n+1)}\beta_{2(n+1)}}{2a_{n+1}},$$

$$\theta_2 x_2 = \frac{\beta_{2(n+1)}^2}{2a_{n+1}},\quad \theta_p x_q = \frac{\beta_{p(n+1)}\beta_{q(n+1)}}{2a_{n+1}},\ \&c.$$

Then we have

$$D' = D - \Sigma\Sigma\frac{\beta_{p(n+1)}\beta_{q(n+1)}}{2a_{n+1}}D_{pq},$$

and by the ordinary expansion

$$\Delta = 2a_{n+1}D - \Sigma\Sigma\beta_{p(n+1)}\beta_{q(n+1)}D_{pq}.$$

Therefore $$D' = \frac{1}{2a_{n+1}}\Delta.$$

(*f*) In this last deduction we have attributed no particular values to the C constituents.

It would therefore hold for all the minors of D' not containing the suffix $n+1$ as well as for D' itself, namely

$$D_{11}' = \frac{1}{2a_{n+1}}\Delta_{11},$$

$$D_{12}' = \frac{1}{2a_{n+1}}\Delta_{12};$$

and therefore

$$\frac{D_{11}'}{D'} = \frac{\Delta_{11}}{\Delta},$$

$$\frac{D_{12}'}{D'} = \frac{\Delta_{12}}{\Delta},\ \&c.$$

(g) Now consider the function ϵ^{-hQ} in which h is any constant, and Q is a quadratic function of n variables u_1, $u_2 \dots u_n$, namely

$$Q = a_1 u_1^2 + b_{12} u_1 u_2 + a_2 u_2^2 + \&c.$$

Let us effect the integration

$$\int \epsilon^{-hQ} \, du_n \text{ between limits } \pm \infty.$$

The terms in Q which contain u_n are

$$a_n u_n^2 + (b_{1n} u_1 + b_{2n} u_2 + \dots + b_{(n-1)\,n}\, u_{n-1})\, u_n,$$

which may be put in the form

$$\left(u_n \sqrt{a_n} + \frac{b_{1n} u_1 + b_{2n} u_2 + \&c.}{2\sqrt{a_n}}\right)^2 - \frac{(b_{1n} u_1 + b_{2n} u_2 + \&c.)^2}{4 a_n}.$$

Let us for a moment write

$$\frac{b_{1n} u_1 + b_{2n} u_2 + \&c.}{2\sqrt{a_n}} = z.$$

Then
$$\int_{-\infty}^{\infty} \epsilon^{-hQ} \, du_n$$

$$= \epsilon^{-hQ'} \frac{1}{\sqrt{a_n}} \int_{\infty}^{\infty} \epsilon^{-h(u_n\sqrt{a_n}+z)^2} \, d\,(u_n \sqrt{a_n} + z)$$

$$= \epsilon^{-hQ'} \text{ multiplied by a numerical factor,}$$

and
$$Q' = \left(a_1 - \frac{b_{1n}^2}{4a_n}\right) u_1^2 + \left(b_{12} - \frac{b_{1n} b_{2n}}{2a_n}\right) u_1 u_2 + \&c.$$

$$+ \left(a_2 - \frac{b_{2n}^2}{4a_n}\right) u_2^2 + \&c.$$

Comparing these results with (e), (f) we see that if

$$D = \left| \begin{array}{l} 2a_1,\ b_{12},\ b_{13} \dots b_{1n}, \\ b_{12},\ 2a_2,\ b_{23} \dots b_{2n}, \\ \dots\dots\dots\dots\dots\dots\dots \end{array} \right|$$

D containing $(n+1)^2$ constituents,

and
$$D' = \left| \begin{array}{llll} 2a_1 - \dfrac{b_{1n}^2}{2a_n}, & b_{12} - \dfrac{b_{1n} b_{2n}}{2a_n}, & b_{13} - \dfrac{b_{1n} b_{3n}}{2a_n}, & \dots, \\ b_{12} - \dfrac{b_{1n} b_{2n}}{2a_n}, & 2a_2 - \dfrac{b_{2n}^2}{2a_n}, & \dots, & \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots & & & \end{array} \right|$$

D' containing n^2 constituents;

then $$\frac{D_{11}'}{D'} = \frac{D_{11}}{D}, \quad \frac{D_{12}'}{D'} = \frac{D_{12}}{D}.$$

That is, these ratios are not altered by the change in the coefficients a_1, b_{12}, &c., consequent on the integration according to u_n. Evidently the same law holds for every subsequent integration. Let us then perform the integrations

$$\iiint e^{-hQ}\, du_3 \ldots du_n,$$

and let the result be

$$\iiint e^{-hQ}\, du_3 \ldots du_n = e^{-h(A_1u_1^2 + B_{12}u_1u_2 + A_2u_2^2)}.$$

If $e^{-h(A_1u_1^2 + B_{12}u_1u_2 + A_2u_2^2)}\, du_1du_2$ is proportional to the chance that two variables u_1 and u_2 shall lie between the limits $u_1 \ldots u_1 + du_1$ for the one, and $u_2 \ldots u_2 + du_2$ for the other, we easily find the mean of u_1^2, thus

$$u_1^2 = \iint e^{-h(A_1u_1^2 + B_{12}u_1u_2 + A_2u_2^2)}\, u_1^2 du_1du_2,$$

the limits of integration being for each u ± ∞

$$= \frac{1}{h} \frac{2A_2}{4A_1A_2 - B_{12}^2} = \frac{d_{11}}{hd},$$

if d be the determinant

$$\begin{vmatrix} 2A_1, & B_{12}, \\ B_{12}, & 2A_2. \end{vmatrix}$$

But $\frac{d_{11}}{d} = \frac{D_{11}}{D}$ by the last article.

Therefore $$\overline{u_1^2} = \frac{D_{11}}{hD}.$$

Similarly $$\overline{u_1u_2} = \frac{D_{12}}{hD},$$

$$\overline{u_2^2} = \frac{D_{22}}{hD},$$

and so on.

(*h*) Under the same circumstances to find the mean value of $\frac{dQ}{du_1}$, or $2a_1u_1 + b_{12}u_2 + b_{13}u_3 + \&c.$, u_1 being given (see Art. 97).

That is to effect the integration

$$\iiint \ldots du_2 \ldots du_n \epsilon^{-hQ} (2a_1u_1 + b_{12}u_2 + \&c.).$$

Let $$2a_1u_1 + b_{12}u_2 + b_{13}u_3 + \&c. = P.$$

The coefficient of u_1 in P is twice the coefficient of u_1^2 in Q. The coefficient of every other u, as u_2, in P is equal to the coefficient of u_1u_2 in Q.

After integrating according to u_n the coefficient of u_1 in P is $2a_1 - \frac{b_{1n}^2}{2a_n}$ while that of u_1^2 in Q is $a_1 - \frac{b_{1n}^2}{4a_n}$.

The coefficient of u_2 in P is $b_{12} - \frac{b_{1n}b_{2n}}{2a_n}$, and the coefficient of u_1u_2 in Q is the same.

The same relation between the coefficients in P and those in Q which existed before integration according to u_n exists also after that integration. The same rule holds for every subsequent integration to u_2 inclusive. But when all the integrations have been effected to u_2 inclusive, Q has become $\frac{D}{2D_{11}}u_1^2$. Therefore P has become $\frac{D}{D_{11}}u_1$ which is the mean value sought.

(*i*) Let us now consider the determinant

$$D = \begin{vmatrix} S^2, & -f_1S, & -f_2S, & -f_3S, \ldots \\ -f_1S, & (1+f_1^2), & f_1f_2, & f_1f_3, \ldots \\ -f_2S, & f_1f_2, & (1+f_2^2), & f_2f_3, \ldots \\ -f_3S, & f_1f_3, & f_2f_3, & (1+f_3^2), \ldots \\ \multicolumn{4}{c}{\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots} \end{vmatrix}$$

treated of in Chapter v, Art. 63. Here S is written for Σf of that Article.

Comparing it with the type determinant, we find

$$C_{11}=S^2, \quad C_{22}=1+f_1^2, \quad C_{33}=1+f_2^2, \text{ \&c.},$$
$$C_{12}=C_{21}=-f_1S, \text{ \&c.}, \quad C_{23}=C_{32}=f_1f_2, \text{ \&c.}$$

Let it be required to find the values of D and its first minors.

(*j*) We observe that in D every row except the top row contains one constituent of the form $1+f^2$, *e.g.* the $(p+1)$th row contains $1+f_p^2$. If it were f_p^2 instead of $1+f_p^2$, the $(p+1)$th row would be similar to the top row and therefore D would be zero.

If we strike out any column other than the first, say the qth column, we deprive the qth row of its constituent $1+f_{q-1}^2$. Hence the qth row is now similar to the top row.

And if, to form a minor, we strike out any other row, neither the first nor the qth, the determinant, *i.e.* the minor so formed, is zero. We see then that if $p>1$, and $q>1$, and $p \neq q$, $D_{pq}=0$. But if we expand D, the constituent C_{pq} appears only in the form $D_{pq}C_{pq}$, and $D_{pq}=0$. Therefore D when expanded does not contain any unaxial constituent except those in the first row or first column.

From (*i*) and (*j*) we see that $D=S^2$. For the same reason $D_{22}=S^2$, and so on for every coaxial minor except D_{11}, but as we shall see later $D_{11}=\Sigma f^2+1$.

(*k*) We have next to find D_{12}, D_{13}, &c. Striking out from D the top row and second column to form D_{12}, we find that in D_{12} every row except the top row has one constituent of the form $1+f^2$. Therefore by the same reasoning as in (*j*) and by the rule as to the sign of the product of the axial constituents, $D_{12}=D_{21}=+f_1S$. When we form D_{13}, the product of the axial constituents is by our rule to be positive. But in order to reduce this minor to one in which the top row does not contain a constituent of the form $1+f^2$, we must interchange the two top rows, and thereby change the sign, of the minor. Therefore $D_{13}=+f_2S$ and so on. In forming any minor $D_{1}p$ we have if p is odd, an odd number of changes of sign.

(*l*) Next let us deal with D_{11}.

Let
$$\Delta = D_{11} = \begin{vmatrix} 1+f_1^2, & f_1f_2, & f_1f_3, & \dots \\ f_1f_2, & 1+f_2^2, & f_2f_3, & \dots \\ f_1f_3, & f_2f_3, & 1+f_3^2, & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix}$$

or
$$C_{11} = 1+f_1^2, \quad C_{12} = f_1f_2, \text{ \&c.}$$

All products of the form $f_p^2 f_q^2$ evidently disappear in expansion, and therefore all terms involving f^2 except in the first degree disappear, and therefore

$$D_{11} = 1 + \sum_1^{n-1} f^2$$
$$= \sum_1^{n} f^2, \text{ if } f_n = 1.$$

(*m*) Again, if we strike out any column except the first, say the second, we thereby deprive the second row of its constituent $1+f_2^2$. And therefore if we now strike out the top row we shall have

$$\Delta_{12} = \begin{vmatrix} f_1f_2, & f_2f_3, & f_2f_4, & \dots \\ f_1f_3, & (1+f_3^2), & f_3f_4, & \dots \\ f_1f_4, & f_3f_4, & (1+f_4^2), & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix}$$

$= -f_1f_2$ by the rule as to the sign of the axial constituents.

Similarly $\Delta_{13} = -f_1f_3$.

Also $\Delta_{11} = \Sigma f^2 - f_1^2$,

$\Delta_{22} = \Sigma f^2 - f_2^2$, &c.

(*n*) In the type determinant let now every C become $C + \partial C$, and let all the ∂C's be small, so that we may neglect products of them. That being the case

$$\partial D = \Sigma \frac{dD}{dC} \partial C$$
$$= \sum_{p=1}^{p=n} \sum_{q=1}^{q=n} \frac{dD}{dC_{pq}} \partial C_{pq}.$$

Let us apply this to the determinant of (i) in which

$$C_{11} = S^2, \qquad C_{12} = -f_1 S, \qquad C_{13} = -f_1 S, \text{ \&c.},$$
$$C_{21} = -f_1 S, \quad C_{22} = 1 + f_1^2, \text{ \&c.}$$

Here as we have seen $\dfrac{dD}{dC_{pq}} = 0$, unless either $p = 1$, or $q = 1$, or $p = q$.

Therefore

$$\begin{aligned} \partial D = D_{11}\partial C_{11} &+ f_1 S \partial C_{12} + f_2 S \partial C_{13} + \text{\&c.} \\ &+ f_1 S \partial C_{21} + f_2 S \partial C_{31} + \text{\&c.} \\ &+ S^2 \partial C_{22} + S^2 \partial C_{33} + \text{\&c.} \end{aligned}$$

Now as in Art. 83 let us make

$$\partial C_{11} = 0, \qquad \partial C_{12} = \tfrac{1}{2} b_{1n} S, \qquad \partial C_{13} = \tfrac{1}{2} b_{2n} S, \text{ \&c.}$$
$$\partial C_{21} = \tfrac{1}{2} b_{1n} S, \qquad \partial C_{31} = \tfrac{1}{2} b_{2n} S, \text{ \&c.},$$
$$\partial C_{22} = -b_{1n} f_1, \quad \partial C_{33} = -b_{2n} f_2, \text{ \&c.}$$

Then as products of the b's are to be neglected, we have

$$\begin{aligned} \partial D &= + b_{1n} f_1 S^2 + b_{2n} f_2 S^2 + b_{3n} f_3 S^2 - \text{\&c.} \\ &\quad - b_{1n} f_1 S^2 - b_{2n} f_2 S^2 - \text{\&c.} \\ &= 0. \end{aligned}$$

(o) Let us treat D_{11}, or Δ, in the same way. Here

$$C_{11} = 1 + f_1^2, \quad C_{12} = f_1 f_2, \text{ \&c.}$$

And
$$\begin{aligned} \partial D_{11} &= \partial \Delta, \\ &= \frac{d\Delta}{dC_{11}} \partial C_{11} + \frac{d\Delta}{dC_{12}} \partial C_{12} + \text{\&c.} \end{aligned}$$

And
$$\partial C_{11} = - b_{1n} f_1, \quad \partial C_{22} = - b_{2n} f_2, \text{ \&c.},$$
$$\partial C_{12} = \tfrac{1}{2}(b_{12} - b_{1n} f_2 - b_{2n} f_1), \text{ \&c.}$$

Therefore, since each anaxial term $f_1 f_2$, &c. appears twice,

$$\begin{aligned} \partial\Delta &= -(\Sigma f^2 - f_1^2)\, b_{1n} f_1 - (\Sigma f^2 - f_2^2)\, b_{2n} f_2 - \text{\&c.} \\ &\quad - f_1 f_2 (b_{12} - b_{1n} f_2 - b_{2n} f_1) - f_1 f_3 (b_{13} - b_{1n} f_3 - b_{3n} f_1) - \text{\&c.} \\ &= - b_{12} f_1 f_2 - b_{13} f_1 f_3 - \ldots - b_{pq} f_p f_q \\ &\quad - \Sigma f^2 (b_{1n} f_1 + b_{2n} f_2 + \text{\&c.}) \\ &\quad + f_1^2 b_{1n} f_1 + f_2^2 b_{2n} f_2 \\ &\quad + f_2^2 b_{1n} f_1 + f_3^2 b_{1n} f_1 + \ldots + f_1^2 b_{2n} f_2 + f_3^2 b_{2n} f_2 + \text{\&c.} \end{aligned}$$

That is
$$\partial\Delta = -b_{12}f_1f_2 - b_{13}f_1f_3 \quad \&c.$$
$$= -\Sigma_{p=1}^{p=n}\Sigma_{q=1}^{q=n}b_{pq}f_pf_q.$$

In this result every $b_{pq}f_pf_q$ is to be counted once only, that is, we do not distinguish b_{pq} from b_{qp}. If $b_{pq}f_pf_q$ and $b_{qp}f_qf_p$ are counted separately, we must write

$$\partial\Delta = -\tfrac{1}{2}\Sigma_{p=1}^{p=n}\Sigma_{q=1}^{q=n}b_{pq}f_pf_q,$$

and this form is the one required in Art. 83.

(p) To prove that for certain values of b, $\Sigma f_p\Sigma b_{pq}f_q = \Sigma f_p^2\Sigma b$ see (33) of Art. 83. Let f (Art. 61) $= \dfrac{1}{r^{n+2}}$ when $r > a$.

Taking O for origin, let p be any point $Op = p$. About p describe a sphere of radius r less than p, and let q be a point on its surface. If $n + 2 = 1$, or $f = \dfrac{1}{r}$, the mean value of f_q for all points q on the sphere is $\dfrac{1}{Op}$, or f_p. And equation (33) is accurately satisfied, so long as $r < p$.

If $n + 2 > 1$, we have in usual notation

$$f_q = \tfrac{1}{2}\int_0^\pi \frac{\sin\theta d\theta}{(p^2 + r^2 - 2pr\cos\theta)^{\frac{n+2}{2}}}$$

$$= \frac{1}{2npr}\,\frac{(p+r)^n - (p-r)^n}{(p^2 - r^2)^n}$$

$$= \frac{1}{npr}\,\frac{np^{n-1}r + \dfrac{n\,.\,\overline{n-1}\,n-2}{2\,.\,3}p^{n-3}r^3 + \&c.}{(p^2 - r^2)^n}$$

$$= \frac{1}{p^{n+2}}\left(1 + \frac{\overline{n-1}\,n-2}{2\,.\,3}\frac{r^2}{p^2} + \&c.\right)\left(1 + \frac{r^2}{p^2} + \frac{r^4}{p^4} + \&c.\right)^{2n}$$

$$= f_p + \text{terms containing } f_p \text{ multiplied by } \frac{r^2}{p^2}\ \&c.$$

And if now $b = -\left(\dfrac{c}{r}\right)^\mu$, where $\mu > 3$,

$$f_p\int_c^\infty 4\pi r^2\rho b f_q dr = f_p^2\int_c^\infty 4\pi r^2\rho b dr = f_p^2\Sigma b,$$

because, $\frac{c}{p}$ being negligible, all the terms in the integral which follow the term $f_p^2\Sigma b$ are negligible compared with $f_p^2\Sigma b$.

(*q*) To find the condition that the quadratic function (*q*)

$$Q = a_1u_1^2 + b_{12}u_1u_2 + a_2u_2^2 + \dots$$

shall be always positive whatever values be attributed to $u_1, u_2 \dots u_n$.

Evidently since $u_2 \dots u_n$ may be all zero, a_1 must be positive. Similarly a_2, a_3, &c., must be positive.

Also, given u_n, Q is minimum when

$$\frac{dQ}{du_n} = 2a_nu_n + b_{1n}u_1 + b_{2n}u_2 + \&c. = 0.$$

And, when minimum, Q must be positive. Substitute in Q for u_n the value found for it from

$$2a_nu_n + b_{1n}u_1 + b_{2n}u_2 + \&c. = 0,$$

that is
$$u_n = -\frac{b_{1n}u_1 + b_{2n}u_2 + \dots}{2a_n},$$

Q then becomes

$$Q' = a_1'u_1^2 + b_{12}'u_1u_2 + a_2'u_2^2 + \&c.,$$

where
$$a_1' = a_1 - \frac{b_{1n}^2}{4a_n}, \quad a_2' = a_2 - \frac{b_{2n}^2}{4a_n}, \&c.,$$

and every a' must be positive. Also $b_{12}' = b_{12} - \frac{b_{1n}b_{2n}}{2a_n}$ &c.

Proceeding in the same way Q is ultimately reduced to $Q = \frac{D}{2D_{11}}u_1^2$, and as this must be positive, $\frac{D}{D_{11}}$ must be positive. Similarly $\frac{D}{D_{22}}$ must be positive, and so on. Therefore D and all its first coaxial minors have the same sign. But if we only reduce Q to a quadratic function of u_1 and u_2

$$Q = \frac{D_{11}}{2D_{1221}}u_1^2 + \frac{D_{12}}{D_{1221}}u_1u_2 + \frac{1}{2}\frac{D_{22}}{D_{1221}}u_2^2.$$

From which and the corresponding equations we see that all the second coaxial minors have the same sign as the first coaxial minors, and therefore the same sign as D.

Similarly we can prove that the third coaxial minors must have the same sign as the second and so on, so that D and all its coaxial minors must have the same sign. And this sign must be positive because a_1, a_2, &c., are coaxial minors. This is the required condition.

(r) Referring to Chapter V, in which it is proved that with (r) spheres of finite diameter c,

$$\frac{dM_{xz}}{dt} = \tfrac{8}{3}\pi c^3 \rho \frac{1}{2h}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2,$$

where $$M_{xz} \text{ or } M = \iiint dxdydz\alpha\gamma\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right),$$

to prove the same thing for

$$M_{xx} = \iiint dxdydz\alpha^2 \frac{d\xi}{dx}.$$

Consider the space between two infinite planes $x = 0$ and $x = dx$, between which $\frac{d\xi}{dx}$ is supposed constant and negative. Let $u = \alpha - \xi$. Then it is proved, as in Art. 64, that the number per unit of volume of molecules for which $\alpha - \xi$ lies between u and $u + du$, when $x = 0$, exceeds the corresponding number when $x = dx$ by the quantity

$$C\epsilon^{-h'u^2} 2h'u \frac{d\xi}{dx} dxdu.$$

Therefore the number which enter the space between the planes exceeds the number which leave it per unit of time by

$$C\iint dydz\epsilon^{-h'u^2} du 2h'u\alpha \frac{d\xi}{dx}.$$

Hence as in Art. 66, it follows that, for each element of volume $dxdydz$,

$$\frac{d}{dt}(u\alpha) = -\iint_{-\infty}^{\infty} C\epsilon^{-h'u^2}\epsilon^{-h\alpha^2}\, 2h'u^2\alpha^2 du\, d\alpha\, \frac{d\xi}{dx}$$

$$= -\overline{u^2\alpha^2}\, 2h'\, \frac{d\xi}{dx}.$$

Now u and α are not independent, as u and γ were in Art. 66. Hence

$$\overline{u^2\alpha^2} = \frac{2h}{2h'}\, \overline{\alpha^4} = \frac{2h}{2h'}\, \frac{3}{4h^2} = \frac{3}{2h'2h},$$

and
$$2h'u^2\alpha^2 = \frac{3}{2h}.$$

Hence
$$\frac{d\xi}{dx}\frac{du^2}{dt} = \frac{d\xi}{dx}\frac{d\alpha^2}{dt} = -\frac{3}{2h}\left(\frac{d\xi}{dx}\right)^2 \text{..............(1)},$$

which corresponds to

$$\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)\frac{d(\alpha\gamma)}{dt} = -\frac{1}{2h}\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2,$$

of Art. 66.

It follows, the motion being stationary, that

$$\alpha^2 \frac{d}{dt}\frac{d\xi}{dx} = \frac{3}{2h}\left(\frac{d\xi}{dx}\right)^2,$$

or by the process of Art. 68

$$-\alpha^4 \frac{1}{r}\frac{df}{dr}(r = a) = \frac{3}{2h}\left(\frac{d\xi}{dx}\right)^2 \text{..............(2)}.$$

When the material points are replaced by spheres of finite diameter c, $\frac{d\alpha^2}{dt}$ acquires a new term due to collisions, which we will denote by $\frac{\partial\alpha^2}{\partial t}$, and we have

$$\frac{d\xi}{dx}\frac{\partial\alpha^2}{\partial t} = \frac{d\xi}{dx}\frac{\partial V_x^2}{\partial t},$$

V_x, V_y, V_z, being the components of the half relative velocity of two colliding spheres.

Also
$$\frac{\partial V_x^2}{\partial t} = 2\pi c^2 \rho V (\lambda'^2 - \lambda^2) V^2,$$

where
$$\lambda V = V_x, \quad \mu V = V_y, \quad \nu V = V_z, \; .$$

and using the same notation as in Arts. 70—71, we find

$$\frac{\partial V_x^2}{\partial t} = \frac{1}{\pi} 2\pi c^2 \rho V 4h \frac{d\xi}{dx} \frac{c}{2} V^3 \lambda \int_0^{\frac{\pi}{2}} d\theta \int_0^{\pi} d\phi 2 \sin\theta \cos\theta$$
$$\times (-\lambda \cos\theta + \sqrt{1-\lambda^2} \sin\theta \cos\phi') \{\lambda^2 (4\cos^4\theta - 4\cos^2\theta)$$
$$+ (1-\lambda^2) \sin^2 2\theta \cos^2\phi' - 2\lambda \sqrt{1-\lambda^2} \cos 2\theta \sin 2\theta \cos\phi'\}$$
$$= 2\pi c^3 \rho V^4 4h \frac{8}{3.3.5} \lambda^4 \frac{d\xi}{dx},$$

whence introducing the factor $C\epsilon^{-2hV^2} V^2 dV$ where $C = \frac{4}{\sqrt{\pi}} (2h)^{\frac{3}{2}}$ and integrating from $V=0$ to $V=\infty$,

we get
$$\frac{\partial V_x^2}{\partial t} = \frac{8}{15} \pi c^3 \rho \frac{1}{2h} \frac{d\xi}{dx},$$

or
$$\frac{d\xi}{dx} \frac{\partial V_x^2}{\partial t} = \frac{d\xi}{dx} \frac{\partial \alpha^2}{\partial t} = \frac{8}{15} \pi c^3 \rho \frac{1}{2h} \left(\frac{d\xi}{dx}\right)^2 \quad \ldots\ldots\ldots(3).$$

We have next to calculate the term

$$\alpha^2 \frac{\partial}{\partial t} \frac{d\xi}{dx},$$

due to collisions. That gives by the same method as that employed in Art. 76

$$\frac{\partial}{\partial t} \frac{d\xi}{dx} = -\frac{1}{\pi} 2\pi c^3 \rho V^2 \int_0^{\frac{\pi}{2}} d\theta \int_0^{\pi} d\phi 2 \sin\theta \cos\theta$$
$$\times (-\lambda \cos\theta + \sqrt{1-\lambda^2} \sin\theta \cos\phi')$$
$$\times (-2\lambda \cos^2\theta + \sqrt{1-\lambda^2} \sin 2\theta \cos\phi') \frac{1}{r} \frac{df}{dr} (r=a).$$

Whence we obtain for a pair of colliding spheres

$$\alpha^2 \frac{\partial}{\partial t} \frac{d\xi}{dx} = -4\pi c^3 \rho V^4 \frac{44}{45} \lambda^4 \frac{1}{r} \frac{df}{dr} (r=a),$$

and for each sphere separately

$$\alpha^2 \frac{\partial}{\partial t}\frac{d\xi}{dx} = -4\pi c^2 \rho V^4 \frac{22}{45}\lambda^4 \frac{1}{r}\frac{df}{dr}(r=a)$$

$$= \frac{22}{15}\pi c^2 \rho \frac{1}{2h}\left(\frac{d\xi}{dx}\right)^2 \text{ by (2) } \ldots\ldots\ldots\ldots(4).$$

Adding this to (3) we find for the change of M_{xx} with the time due to collisions

$$\frac{\partial M_{xx}}{\partial t} = \frac{30}{15}\pi c^2 \rho \frac{1}{2h}\left(\frac{d\xi}{dx}\right)^2$$

$$= 2\pi c^2 \rho \frac{1}{2h}\left(\frac{d\xi}{dx}\right)^2.$$

Using M_{xx} for M_{zz} or M in Art. 79, we find

$$\alpha^2 \frac{d}{dt}\frac{d\xi}{dx} - \frac{3}{2h}\left(\frac{d\xi}{dx}\right)^2$$

$$+ 2\pi c^2 \rho \frac{1}{2h}\left\{\left(\frac{d\xi}{dx}\right)^2 + \left(\frac{d\xi'}{dx}\right)^2\right\} - \frac{3}{2h}\left(\frac{d\xi'}{dx}\right)^2 = 0$$

The first line is zero. The second can be made zero by making $\left(\frac{d\xi'}{dx}\right)^2 : \left(\frac{d\xi}{dx}\right)^2 :: \kappa : 1 - \kappa$ as before.